A HISTORY OF CHEMISTRY

BY

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LONDON
EDWARD ARNOLD
41 & 43 MADDOX STREET, BOND STREET, W.
1907

TRANSLATOR'S PREFACE

This short history is intended to supply students of chemistry with an outline of the general development of the science. After taking this wide survey of the field the reader will be in a position to profit by the study of individual researches as recorded in the original papers. In the later portion of the book references have been given to several classical papers which should be consulted. In connexion with the work of earlier periods, the *Alembic Club Reprints* may be mentioned as supplying in a convenient form reprints and translations of important papers on the theory of combustion, the elementary nature of chlorine, and other prominent *streitfrage* of former generations which are not readily accessible. These may be supplemented by Ostwald's *Klassiker*, which are a series of reprints of similar character.

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May 28, 1907.

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HISTORY OF CHEMISTRY

PART I

INTRODUCTION

ALTHOUGH nowadays we understand by chemistry the study of inorganic and organic substances, of their transformation products, and of the laws according to which these are formed, we should by no means fall into the belief that this has always been the underlying principle of chemistry. On the contrary, chemical science had a lengthy path to traverse before it won its way to this position. We find that chemistry has followed various guiding principles at different periods, and that these have determined the direction of chemical work for tens or hundreds of years at a time. On this account there have arisen in the historical development of chemistry definite periods completely dominated by some one leading idea.

In ancient times we may notice (apart from the philosophical speculations of Aristotle and his disciples) an empirical treatment of chemical processes, in which the endeavour to make economic use of them takes a prominent place. The suc-

ceeding period, from the fourth to the sixteenth centuries after Christ, is completely ruled by that notion of the transmutation of the metals which was the mainspring of alchemistic effort. Although this idea has been running in the heads of chemists even up to our own time, its hold upon their minds was loosened in the seventeenth century by the endeavour to place chemistry in the service of medicine.

With the eighteenth century there began a further change, through which chemistry developed itself from the position of a subordinate science to its present independence. It was, above all, with the significance of the process of combustion that the chemists of that time were deeply occupied, and its correct explanation by the Frenchman Lavoisier gave to the next period—which includes the end of the eighteenth and the beginning of the nineteenth century—its distinctive mark. In the year 1828 a new course was indicated by Wöhler, professor of chemistry at Göttingen, for he was the first to prepare synthetically the substance urea, a product of the animal body. Then followed, one after another, discoveries and syntheses of organic compounds, which were required to furnish the material for the theoretical developments. The synthesis in the year 1856 of an artificial dyestuff formed the foundation of the organic dyestuff industry, which has now reached so great a development; and with the help of this, general chemical industry, in common with the preparation of artificial drugs and the necessary

raw materials, has been worked up into an economic factor of the first importance. In theoretical chemistry a useful form of the molecular and atomic theory was obtained towards the middle of the century, and the year 1886 brought a new change with the introduction of the dissociation theory of Arrhenius. All inorganic reactions were regarded as 'ionic' reactions, and by the aid of the law of mass action, which is so important in the study of the progress of reactions, we have reached the present standpoint of chemistry—to seek the laws according to which chemical reactions occur. This has given new life to the doctrine of chemical affinity already indicated by Geoffroy, which in this new form, founded on the principle of the conservation of energy and mathematically developed, is exerting itself exactly to describe chemical processes. In all cases now the chemist no longer asks merely *what* is formed in a reaction, but his inquiry goes further: he wishes to be informed *how* that is produced, and, as a consequence, *why* it is produced.

For the sake of clearness of treatment of the historical development of chemistry, the division into periods mentioned above will be retained in the more complete consideration of the subject. The first part will treat of the development as far as the theory of combustion of Lavoisier—*i.e.*, to about the year 1774; while in the second part will be described the whole development of chemistry from the standpoint of quantitative investigation. The first part is therefore divided as follows:

1. Chemistry of the Ancients, to the fourth century A.D.

2. Period of Alchemy, from the fourth to sixteenth centuries.

3. Period of Iatrochemistry, sixteenth and seventeenth centuries.

4. Period of the Phlogiston Theory, 1700-1774.

CHAPTER I

THE CHEMISTRY OF THE ANCIENTS

CONCERNING the chemical knowledge of the ancient peoples we possess only very scanty information, derived from the Egyptians, Phœnicians, Israelites, Greeks, and Romans. In respect to its reliability and credibility great care is required, for really certain data only exist in the case of the Greeks and Romans. The reason for this is to be found chiefly in the fact that the scientific study of the teachings of Nature was the privilege of particular classes of the population, and was kept strictly secret from the common people.

In addition to written remains, however, discoveries made in the most varied excavations furnish us with evidence that the technical employment of certain chemical processes was fairly well developed, although with no complete comprehension of the real chemical changes involved. Here there need be recalled only the manufacture of glass and the working of the metals ; both of these operations seem to have been carried out in a much more complete manner among the Egyptians and

Phœnicians than is to be noticed several hundred years after among the Greeks.

The scientific treatment of chemistry suffered under a general misfortune, which is noticeable to some extent even as late as the seventeenth century of our era, and which was, that *experimental* investigation, though not quite omitted, was practised only in the most extremely limited way. For this reason chemical research during this period lay entirely in the hands of the philosophers, and was considered from a purely philosophical, speculative point of view, without any reliance on facts based upon experience.

A praiseworthy exception to this seems to have been (according to several historians) the well-known philosopher Democritus of Abdera, who lived in the fifth century B.C., and is reported to have spent his life in experimenting. At a later date, in the middle of the first century A.D., one Dioskorides, a physician of Anazardai in Asia Minor, seems to have possessed a noteworthy knowledge of the preparation of drugs and of chemical manipulations. He gave in his *Materia medica* a series of instructions relating to chemical operations, such as the extraction of mercury from cinnabar or the roasting of raw antimony; we also find mention in his work of a kind of distillation. By far the most comprehensive account of the chemical knowledge of antiquity is left us in the thirty-seven books of the *Historia Naturalis*, by Caius Plinius Secundus, who was born in A.D. 23 at Verona, and lost his

life in the eruption of Vesuvius in the year 79. In the time after Pliny we find some remains of the physician Claudius Galenus (Galen), which bring us nothing essentially new on chemical matters; their author was born in A.D. 131 at Pergamos in Asia Minor, and received his medical training in Egypt. None of those who busied themselves with chemistry during this period understood how to turn their experimental experiences and observations to good account by the inductive method: in their theoretical views they always fell back upon deduction. The leader of the ancients in scientific matters was the Greek Aristotle of Stagira (384-322 B.C.). He maintains the view (which is derived from Indian, and eventually from Chinese, speculations, and is in agreement with those of the philosopher Empedocles) that substances in their ultimate constitution are composed of elements, and these he regards as the things into which all substances when split up are resolved. The elements themselves are capable of qualitative change, and are to be regarded as potentially present in the substances. A mixture of these elements in reality constitutes a substance. The transformation of one substance into another is brought about by a separation of the substance into its elements, and the mixing of these in a new arrangement. As elements of this kind he designated air, water, fire, and earth, and held it possible for these to change among themselves. His doctrines in these matters rest on purely speculative ground, in spite of the fact that in other

places he maintains the view that facts must first be discovered, and all conclusions drawn from them. We are to suppose that the 'Aristotelian doctrine' of these elements did not see in them the original constituents of matter, but indicated thereby only certain states of matter, its fundamental properties. His endeavours went so far as to seek for certain properties of matter common to the whole. It is clear *a priori* that only the sensible properties were adduced to this end. For him the elementary properties were such as 'moist,' 'wet,' 'cold,' 'warm,' 'dry,' 'heavy,' 'light,' 'hard,' 'soft,' and so on. Among these he distinguished as the special ultimate properties, according to his idea, 'hot,' 'cold,' 'dry,' and 'moist,' and supposed that an element possessed two of these properties, one of each kind. An element may therefore be 'dry and hot,' 'moist and cold,' but not 'moist and dry,' 'cold and hot,' at the same time. In this way he obtained four elementary conditions of matter, and termed that of dryness and heat 'fire,' that of heat and moisture 'air,' that of moisture and cold 'water,' and that of cold and dryness 'earth.' It soon became apparent, however, that these four elements were not sufficient, and so he assumed in the universe a fifth element, to which he ascribed a higher ethereal nature. By this he meant much the same thing as was understood in the Middle Ages by the term *quinta essentia*.

With the help of his four elements he defined also the conception of the solid state as a combina-

tion of dryness and cold, which might, however, be removed by an opposite combination, such as that of moisture and heat; in this way he sought to explain the process of solution or fusion.

Of more purely chemical processes treats Theophrastus, a pupil of Plato and Aristotle, who was born in 371 B.C. on the island of Lesbos, and died at Athens in 286. His papers extend chiefly over the chemistry of minerals, as may be perceived from the title of his book *Περὶ Λίθων*. He gives information about cinnabar, arsenic sulphide, and the preparation of white lead and red lead; here also we find the first mention of coal.

The Gases, Air, and Water.

The ideas of the nature of gases were not very well defined among the ancients. Pliny, for instance, probably in accordance with the Aristotelian doctrine, terms the air an element which tends to rise upward, as against earth and water, which have a tendency to move downward. In contradiction to this, however, Vitruvius, who was military engineer under Cæsar and Augustus, and was occupied in many ways with mechanics, waterworks, and machines, ascribes to air a certain weight which exerts a pressure downwards, for only by this means could he explain the rising of water in pumps. On the chemical composition of air the old chemists did not endeavour to form any ideas, and their knowledge of the nature of other gases was also very small.

Water, on the contrary, occupied them to a correspondingly greater degree. The supposition of a series of philosophers especially deserves mention: that by condensation there could arise from water solid matter—*i.e.*, according to their views, earth. Diodorus (30 B.C.) said, for instance, that rock-crystal had been formed from the purest water by the action of heavenly fire. On the same subject the view was expressed by many that it had arisen from water, not by the action of heat, but of continued cold, as the term *χρύσταλλος* (ice) indicates.

THE METALS.

Much further developed was the purely empirical knowledge of the ancients on questions of technical chemistry, and in particular the working of the metals takes a prominent place. The name 'metal' is derived, according to Pliny, from the fact that they never occur alone, but always together (*μετ' ἄλλα*). Among the Israelites six metals are mentioned—gold, silver, copper, iron, lead, and tin. Although concerning the origin of the metals and of the ores containing them the wildest notions prevailed, we find in Pliny and Dioskorides comparatively accurate information on their extraction from the corresponding ores. Gold and silver were probably the earliest known, on account of their occurrence in the massive state, and of the ease with which they could be worked. **Gold** was found in the time of

the Egyptians, principally in Nubia; the Phœnicians got it from the golden land of Ophir, which is probably to be sought in India or Arabia. The extraction of gold by agitation of the crushed ore with water, by washing gold-bearing sand in running water, and by amalgamation, was known to the ancients. Among the properties of gold, Pliny makes mention of its extraordinary ductility, and the gilding of objects which this renders possible.

Silver, probably introduced by the Phœnicians from Armenia and Spain, was at a very early date purified by fusion with lead; a separation of silver and gold, on the other hand, seems not to have been known.

The knowledge of **Copper** also dates from the farthest antiquity. The place in which it was chiefly found was the Isle of Cyprus, from which it obtained its name of *aes cyprium*. It was mainly used in the form of its alloy with tin as 'bronze' for the making of weapons, ornaments, and the like, and that, indeed, at a time before pure tin had become known. Some compounds of copper, such as cuprous oxide and blue vitriol, were known, at least in Pliny's time, and he gives accurate prescriptions for their preparation.

Iron was early prepared by fusion in furnaces from its ores—hæmatite and magnetic iron ore. The Egyptians were further acquainted with the hardening of iron—*i.e.*, with the production of steel,

and its power of becoming magnetic when rubbed with a magnet is mentioned in Pliny.

Tin was fetched, so we are told, from the islands of the Atlantic Ocean, probably Britain, and conveyed in vessels covered with skins.

Lead is mentioned in the books of the Old Testament,[1] and was termed μόλιβος by the Greeks. Pliny describes a separation of lead from tin and silver by melting; the first stream which runs from the furnace is tin (*stannum*), the second is silver, and the residue is litharge. Of the compounds of lead there were known litharge (*lithargyrum*), as well as red lead, called minium or minium cinnabar, and lead carbonate (*cerussa*). Minium was already at that time obtained by heating white lead to redness.

In **Zinc** we have a similar case to that of tin, for pure zinc is only mentioned comparatively late, under the name *cadmus*, while its alloy with copper, brass, became known in the earliest times.

Mercury is termed 'liquid silver' by Theophrastus (about 300 B.C.), and he prepared it by treating cinnabar with copper and vinegar. In Dioskorides we find the distillation with iron as a method for its preparation, and the purification of the raw metal by pressing through leather is recommended by Pliny. It is interesting, besides, that Pliny makes a distinction between that naturally occurring and that artificially obtained. That Pliny

[1] Exodus xv. 10; Job xix. 24.

was quite aware of the ease of amalgamation with other metals follows from the fact that he speaks of the eating away of lead vessels by mercury.

Sulphur is mentioned by Homer as a fumigant, and was possibly used as such for many religious purposes. Its source even then was the volcanic Lipari Isles between Sicily and Italy. Pliny prepared it by melting out from sulphureous earth, and Agricola by roasting sulphureous ores. Under the influence of the school of Galen it found extensive use in medicine.

Acids, Bases, and Salts.

Among acids the ancients knew only acetic acid in the form of vinegar, and they had no definite ideas about its properties as an acid. Nevertheless, it was known even to the Israelites that earth upon which vinegar was poured effervesced, and was dissolved. This solvent power of vinegar probably also led to the legendary story that Hannibal in his march across the Alps cleared away the rocks with vinegar.

Equally scanty is the information concerning alkaline substances. This extends in the main to the description of the extraction of potash from the ashes, and the power of this substance to dissolve oil, to combine with sulphur, and to destroy the colour of green plants. In addition, soda of natural occurrence was largely employed in the manufacture of glass, which will be described later.

The salts resemble the acids and bases in the scanty nature of the knowledge possessed of them. We find various ones mentioned in the old writings. Apart from soda and potash, mentioned above, common salt was known in the very oldest times, and was prepared by evaporation of sea-water in 'salterns' or 'brine-pans' by the heat of the sun, or by pouring sea-water on to burning wood, in which process the nature of the wood used seems to have had a considerable influence on the quality of the salt. Oak-wood and hazel-wood were recommended as preferable, since their ashes possessed the powers of the salt without further treatment.

Alum is mentioned in Herodotus in the eighth century B.C., but only the naturally occurring, not the artificially prepared, product seems to have become known, for Pliny speaks of it as a naturally occurring salt-juice of the earth. It found its chief use in the mordanting of wool and in the preparation of leather, but it was also much employed by the physicians as a medicine. The saltpetre which was known to the Romans seems not to be identical with ours; Pliny's statements about his *nitrum* are, however, very confused and obscure.

Copper vitriol was obtained from mineral waters, and was used by the Romans as shoemaker's-black. It also found employment in medicine; Pliny and Dioskorides mention its emetic properties.

Glass Manufacture.

We have just seen that soda and potash were generally known even in the earliest times, and this has a close connexion with the production of glass, for without these two substances its manufacture is impossible. We find in Pliny the first exact prescription for the preparation of glass by melting together soda and sand. From various discoveries in the Egyptian tombs we are forced to the belief, however, that the production of glass was developed early and comparatively completely among this people, and that they understood very well the preparation of coloured glasses, as well as of enamels and artificial precious stones. Besides the production of glass, the ancients were acquainted with the manufacture of earthen vessels, and it appears that the Etrurians reached a high level in the ceramic industry. While the Chinese, even in the time before the birth of Christ, were well acquainted with the manufacture of porcelain, and employed it for utensils, we do not find either among the Oriental peoples or among the Greeks and Romans any indication which would lead to the conclusion that the working of this branch of the silicate industry had become familiar to them.

Dyeing.

As in the manufacture of glass, so also in dyeing, the Phœnicians and Egyptians had acquired comparatively great skill. The fixing of certain dyes

on to the fabrics with the aid of mordants (especially alum) was in general well known. As colouring matters were employed purple, which was mainly worked up by the Phœnicians, as well as (according to Pliny) white lead, cinnabar, red lead, smalt, verdigris, iron oxide, lamp-black, antimony sulphide, realgar, orpiment, lead sulphide, and indigo. These substances were used both as dyes and as pigments.

The remark made above, that the ancients were acquainted with the solubility of the fats in potash and soda, is in agreement with the fact that even in the earliest times soaps had been prepared by means of this reaction. A distinction was even drawn between hard and soft soaps, according as soda or potash had been employed in their preparation.

From the physicians of the time chemistry received, on the whole, no great advancement. Even though they did make use of some chemical preparations as medicines, they limited themselves for the most part to the administration of plant extracts, without any relation to chemistry. Nevertheless, the practice of medicine was closely connected, even at that time, with so many chemical manipulations that one is justified in saying that the beginnings of pharmaceutical chemistry reach back into the oldest times.

Besides the decomposition of fats with potash and soda, that with litharge was also known, and was used for the preparation of plasters. Of the other

chemical preparations of that time there were used in medicine alum, soda, white lead, verdigris, iron-rust, sulphur, and copper vitriol.

In the province of organic chemistry the preparation of sugar from wheat-starch was known, as well as the extraction of turpentine by distillation from pine-resin, and the preparation of a series of fatty oils by pressing seeds and fruits. To these last belong especially olive-oil, almond-oil, and castor-oil.

CHAPTER II

THE PERIOD OF ALCHEMY

In the preceding chapter we have seen that in antiquity no definite direction is to be found in chemical work ; we shall find in this chapter, however, that with the fourth century after Christ a change set in. The endeavour to effect the transmutation of the metals became the chief centre of interest, and the work of most chemists was influenced by this idea in a striking manner. The period of time during which chemistry lay under this influence extends from the fourth to the middle of the sixteenth century A.D. It is specially designated the period of alchemy.

From various references in the oldest historians it may be plainly recognized, indeed, that the first beginnings of alchemy reach back into grey antiquity, but only at the epoch mentioned did the alchemistic idea come to define the prevailing views of chemistry. There have been isolated alchemists much later, and their traces extend even to our own time, so that, strictly speaking, the duration of alchemistic effort cannot be exactly defined.

THE PHILOSOPHER'S STONE.

The activity of the alchemists revolved round the discovering of the 'philosopher's stone'—the *lapis philosophorum;* for in their opinion there should be a substance which would possess the power, when brought into contact with fused base metals, like copper, lead, or tin, of turning them immediately into gold. Most of the alchemists, in addition to this transformation, supposed a simultaneous increase in weight, and to the substance were ascribed, besides, a whole series of very mystic properties, of which here there may be mentioned only that many alchemists were persuaded that they could effect by its aid a lengthening of human life. Besides the term 'philosopher's stone,' there is also to be met with the expressions 'the great elixir,' 'the great magisterium,' 'the red tincture,' or 'the medicine of the third order' (Geber).

It is of course clear that by the idea of simply and cheaply obtaining with the philosopher's stone gold, at all periods so highly prized and so necessary, the door was opened to deceitful manipulation and trickery. As, in fact, a series of such cases exist, the idea arose that alchemistic processes in general were to be regarded as a mass of pure deception. It should not, however, be forgotten that the alchemists belonged entirely to the Aristotelian school, and Aristotle declares plainly in his teachings that he is persuaded of a transformation of his elements among themselves.

The whole system of Aristotle is permeated with the idea that substances are composed of various properties, such as cold and dry, or hot and moist, etc., and it is quite intelligible that the idea should arise that gold actually consisted of yellow and lustrous, or other concepts of that kind. Nothing was therefore more natural than that gold should be obtained on bringing together substances which showed these properties, and the alchemists sought in various ways to effect its preparation from sulphur and mercury. As, however, this turned out to be not so simple as it seemed, it was supposed there was needed something besides of unknown nature, and that it was which was meant, as an unknown something, by the term 'philosopher's stone.' Such notions would then receive considerable support from the possibility of preparing alloys resembling gold or silver. It was known, for instance, that copper took on by addition of zinc a golden yellow, by addition of arsenic a silver-white colour; and that such alloys were in early times generally regarded as transformations is plainly to be seen from a remark of Geber in the eighth century. Geber calls attention to the fact that copper stands between gold and silver, and can be changed into either of these—a statement which may be readily understood from what has been said. With the advance in the recognition of chemical facts, however, it was then soon noticed that the gold so obtained was not identical with real gold. Then it was sought to realize the attractive idea

of making gold and silver in another way, and here the aid of the mystic essence, the philosopher's stone, was called in.

We should not, however, overlook the fact that, in spite of the fruitlessness of the experiments to transmute the metals, a considerable extension of general chemical knowledge is to be observed in this period. The reason for this is that the investigators of the time did regard experiment as the foundation of investigation—perhaps in a limited degree, yet quite perceptibly. This is shown by the familiarity of the workers of that time with many aids to experiment, such as the operations of filtration, distillation, and sublimation, and the use of various water- and ash-baths. On the other hand, the comprehension of chemical processes was very slight ; only rarely does one find any effort at an explanation of them, and when this does happen the explanation is never free from hypothesis.

The place where alchemistic studies were most practised in early times was Egypt, especially the school of the Alexandrians. All that we know of the alchemy of the fourth to sixth centuries A.D. is founded upon the written remains of the members of this school. Further, some papers of the fourth century, due to Zosimos of Panopolis, have been preserved for us. His writings, which are for the most part composed of secret mystic receipts, were greatly esteemed by the latter alchemists, and seem to have had a directing influence on the alchemistic tendencies of the Middle Ages. From the time about

the end of the fifth century—that is, at a time at which the alchemistic studies of the Alexandrians seem to have been at their highest point—we possess some works by Synesios, the well-known Bishop of Ptolemais, as well as some by Olympiodor. In these also there are few accounts relating to purely chemical matters.

At the end of the seventh century the Egyptian centres of culture, and with them the Alexandrian library, fell a prey to the destroying rage of the invading Arabs. The ease with which this race in a comparatively short time possessed itself of the knowledge of the lands it had despoiled render it possible that the acquisitions of the Alexandrian school were not lost. So we find as early as the middle of the eighth century in Spain, then ruled by the Arabs, a number of centres of art and learning, visited by the seekers after knowledge of all nationalities. Besides medicine, mathematics, and optics, with which the learned men of the time occupied themselves, alchemy was eagerly practised in the Spanish schools.

Biographical.

The greatest repute among the alchemists of that period was possessed by the Arabian physician, Abou Moussah Dschafar al Sofi, called 'Geber' by the people of the West. There exists a whole series of his alchemistic works, which, however, only became generally accessible, in Latin translation,

in the course of the sixteenth century. Consciously or unconsciously, much new matter became incorporated with these writings in the process of translation, so that it is certainly more than doubtful whether everything ascribed to Geber does really come from him. Nevertheless, he appears to us as a man of wide chemical knowledge, if one does not regard the theoretical explanation of chemical processes, concerning which he is in as bad a case as his contemporaries. From Spain alchemy then found its way through France and Italy to Germany and the Slav empires, and we find in Germany the first certainly known alchemist about the year 1063 at the Court of Adalbert of Bremen.

The most important alchemists were Albertus Magnus, Roger Bacon, Arnaldus Villanovanus, and Raymund Lully. These men, who lived about the thirteenth century, followed Geber closely in their opinions. A great number of their writings exist, but these, like those of Geber, seem to have been much enlarged at later dates.

Albertus Magnus, whose real name was Albert von Bollstädt, was born in 1193 at Lauingen, on the Danube. He taught publicly, at first as a Dominican monk in various towns of Germany and France, and became in 1260 Bishop of Regensburg; he retired, however, in 1265 to a Dominican monastery, and died in one at Cologne. Among his numerous writings, *De Alchymia* and *De Rebus Metallicis et Minerabilibus* deserve special mention.

Roger Bacon was born about the year 1214 in the county of Somerset. He also was from the beginning of his life a theologian, and acquired his knowledge at Oxford and Paris ; his many-sided and astonishing knowledge gained him the title of *Doctor Mirabilis.* He pursued mainly the conscientious and well-considered working-out of experiments, and so imprinted upon chemistry a character peculiar enough at that time, but one which was of decisive influence upon its later development. His life was full of persecutions and punishments; he died probably in the year 1294.

Arnaldus Villanovanus lived in the second half of the thirteenth century as a physician at Barcelona. As his teachings gave offence to the spiritual authorities there, he had to fly, and found, after long wanderings in French and Italian towns, protection and support at the Court of King Frederick II. in Sicily. He possessed considerable practical chemical knowledge, and by its aid advanced the art of medicine in his time not inconsiderably. In the year 1313 he perished by shipwreck on his way to Avignon, at the call of Pope Clement V., who lay seriously ill.

Raymund Lully was probably born about 1235, the scion of a noble Spanish house. He spent his youth in dissipation at the Court of Aragon, until in his thirtieth year he devoted himself to science, in consequence (according to his own statement) of a holy vision. To him belong various prescriptions

for the transmutation of the metals, but they are extraordinarily uncertain and obscure. It is certain that of the writings ascribed to him a whole series was not compiled by him, so that historical criticism is here in a difficult position. According to various accounts, he seems to have occupied himself in his old age with the conversion of the unbelievers in Africa, and as a result to have met his death by stoning about the year 1315.

Besides the learned men mentioned above, there were in the fourteenth century in various countries a large number of people who went by the name of alchemists, but neither their works nor their writings brought any valuable extensions of chemical science. The disturbed financial conditions of many European States gave occasion for many Princes of that period to maintain private alchemists with the idea of relieving their need of money when the transformation of base metals into gold had been made possible. It does not need to be specially mentioned that these people alone really deserve the name of 'gold-makers,' and that it was they who chiefly used alchemy the better to conceal trickery and swindling. For how often were these people in the position of losing their well-paid places if they did not show a proof of their skill! What was wanted was then found: the way to it was a small matter. It should not therefore excite astonishment that the result of such alchemistic efforts was continually to lower the repute of chemistry and increase contempt for it from day to day.

New life was brought to this ruinous state of affairs in the second half of the seventeenth century by **Basil Valentine,** and with him occurs also the transition into a new period of chemistry—that is to say, a change in the prevailing views of the science. Of the real life of Valentine we know extremely little. He was a Benedictine monk, born in Upper Germany. His works were published at the beginning of the seventeenth century at Frankenhausen, in Thüringen. Among them his monograph on *Antimony* claims special interest. In his chemical knowledge he stood completely upon the ground of the alchemists, but he worked for the coming period of iatrochemistry in his endeavours to introduce a series of chemical preparations into medicine.

If, as has been pointed out at the beginning of this chapter, the object towards which the alchemists strove was the transmutation of the metals, the question of their composition must necessarily have been decided beforehand. This seems not to have caused much worry to the earlier chemists, for we find the first statements on the point in Geber's work, *Summæ Perfectiones Magisterii*; and it certainly gave the lead to all later views in this direction. These explanations of the constitution of the metals are greatly influenced by the observation that mercury unites extremely easily with other metals to form so-called amalgams, for Geber expresses the opinion that all metals contain mercury.

The amalgams themselves he terms solutions in mercury of the metal concerned, but supposes at the

same time that the latter dissolves only such substances as are similar to itself. Besides mercury, the metals contain, according to him, sulphur, and the differences of the metals among themselves are conditioned by the varied content of mercury and sulphur. The noblest metals, such as gold and silver, contain much mercury and little sulphur, and both in great purity. Accordingly, there should be a means by which the excess of the two constituents over the composition of gold could be removed, and such a means the philosopher's stone must be. From this point of view the latter might be regarded as a ferment, which on addition, by a kind of fermentation, would cause the separation of the constituent present in excess, until the composition of gold was reached. That was, in the main, apart from certain smaller variations and extensions, the prevailing view of the constitution of the metals during the whole period of alchemy. Such variations we find, for instance, in Albertus Magnus, who supposed arsenic, water, and sulphur to be the constituents of the metals; or in Raymund Lully, who not only conceived the metals as consisting of mercury and sulphur, but ascribed these two constituents to all substances. Grave doubts were expressed on these hypotheses from many quarters, and to overcome these their supporters went further and further into speculation, so that the thesis was maintained that the substances mercury and silver regarded as constituents of the metals were not identical with the known

substances of those names. The same opinion held, of course, for the 'salt' introduced by Basil Valentine as a further constituent of the metals. He understood rather by that term everything solid and stable against heat, as opposed to sulphur, which he regarded as the combustible principle, and to mercury, which was that of volatility and of the metallic characteristics. A generalization of these views led them also to the supposition that all substances were composed of these three fundamental substances.

The Gases.

The knowledge of gases, and in particular of the air, made little progress in this period, though a distinction was drawn between combustible gases and non-combustible, between those which could be breathed and those which could not. From this it follows that, though some investigations and observations on various kinds of gases were made, on the whole no advance took place. Basil Valentine describes the gas found in mines, which he names '*Wetter*,' and considers it to be air rendered impure 'by something dense which is injurious to man.' Escapes of gas in chemical operations were generally neglected ; sometimes mention is made of them, but they are then regarded as escapes of imprisoned air.

The Metals.

The number of known metals had been increased towards the end of the alchemistic period by arsenic,

antimony, bismuth, and zinc. The extraction of gold was still carried out as in antiquity, as was that of silver from its ores by the aid of lead. Valentine terms this method '*Ausseigern*.' For the separation of gold from silver, which was in earlier times, as has been mentioned, numbered among the most difficult operations, the cementation process (which was due to the ancients) was still employed in isolated instances at the beginning of this period; but at the time of Albertus Magnus we find definite directions for their separation in the wet way by means of nitric acid. The metallurgy of iron, lead, tin, and copper experienced no essential improvements. The extraction of mercury was undertaken by the alchemists on the large scale with improved apparatus, after the discovery of the rich mercury-mines of Idria and Carniola in the fifteenth century. There is also in Basil Valentine an account of the preparation of mercury from sublimate by distillation with quicklime. Zinc, bismuth, and antimony are often mentioned by Valentine in his writings, and he even dealt with antimony and its compounds in a special treatise under the title *Der Triumphwagen des Antimonii*. Albertus Magnus speaks of arsenic as 'regulus,' and of its oxide, 'white arsenic,' and he describes also its separation from the ores by sublimation. The first reliable account of the knowledge of arsenious acid is found in the eighth century in Geber, who prepared it by burning arsenic sulphide and collecting the sublimate. The compound was generally known to later alchemists, and its

poisonous properties are also often pointed out. The change which the various metals suffer on heating was not overlooked. On this account we often find mention of mercuric oxide, as well as of iron oxide, copper oxide, and arsenious acid. Copper sulphide and mercury sulphide, as sulphur compounds, are often found in alchemical writings, and the solubility of sulphur itself in caustic alkalies, and its precipitation with vinegar as milk of sulphur, were observed.

Acids, Bases, and Salts.

Among the ancients, as we have seen, the only acid known was vinegar; in this period, however, the number of representatives of this class of substances was considerably increased. Sulphuric acid, hydrochloric acid, and nitric acid were familiar substances to the alchemists, and were used to a large extent in chemical operations. Sulphuric acid was prepared in various ways. Geber made it, for instance, by strongly heating alum; Basil Valentine obtained it by distilling iron vitriol mixed with flints, and speaks also of the oxidation of sulphur to sulphuric acid by saltpetre with evolution of light and heat. Nitric acid was obtained by Geber by distilling a mixture of saltpetre, copper vitriol, and alum; while later alchemists prepared it from saltpetre and sulphuric acid. The names *aqua dissoluta* and *aqua fortis* for this acid are due to Geber. Hydrochloric acid is first mentioned in Basil Valentine, who obtained it

by heating a mixture of common salt and iron vitriol, and gave it the name *spiritus salis* (spirit of salt). Its power of dissolving many metals and their oxides was well known to him. *Aqua regia* was known to Geber, and was obtained by him by dissolving sal ammoniac in nitric acid; it is mentioned as a mixture of hydrochloric and nitric acids by Basil Valentine, who gave it the name *aqua regia*. Its solvent action on gold did not escape the alchemists, and they imagined they possessed in it the eagerly sought for 'alkahest,' the universal solvent; not only did it dissolve (or 'consume,' as they expressed it) all metals, including gold, but also other substances, such as sulphur.

Along with the acids the number of known bases also experienced a considerable increase, for the preparation of caustic alkalies by boiling soda and potash solutions with quicklime was known. There is every appearance that these substances were subjected to a complete investigation, for there is mention in the writings of Basil Valentine of a reciprocal action between acids and bases.

Much the greatest increase is, however, to be noticed in the number of salts, and some of them were also frequently and exactly investigated. To the salts of the alkalies already known there were added in particular ammonium carbonate and sal ammoniac. The alchemists of the thirteenth century called the former the 'volatile alkaline salt,' or *spiritus urinæ*, because they made it by distillation of putrefying urine. To Basil Valentine its prepara-

tion from sal ammoniac and alkaline carbonates was also known. Sal ammoniac was obtained partly as a natural product of volcanic origin, partly by heating horse-dung. Its name comes from Geber's *sal armeniacum*, or the *sal armoniacum* of Basil Valentine, while the *sal ammoniacum* of the ancients was ordinary rock-salt.

Alum was chiefly prepared from alum shale in the town of Rocha, and was purified by recrystallization from water. The power of *aqua regia* to dissolve gold made gold chloride accessible; it possessed extraordinary interest for the chemists of that time, since as *aurum potabile* they ascribed to it the most powerful medicinal action. By solution of silver in nitric acid the alchemists obtained silver nitrate. The precipitation of solutions of it by common salt solutions did not escape their observation, but here also, as was so often the case, they did not understand how to seek an explanation of the chemical process by way of the facts alone, with the exclusion of all hypothesis. In this period also the separation of silver from its solutions by means of mercury or copper was carried out in various ways. Among mercury compounds, mercuric chloride (corrosive sublimate) was prepared by Geber by heating mercury with salt, alum, and saltpetre; and Basil Valentine recognized hydrochloric acid as a constituent of it, without, however, drawing any further conclusions.

It appears that corrosive sublimate was at that time a chemical preparation pretty much in request,

for, as may be concluded from several references, it even then formed an article of commerce. Geber also mentions mercuric oxide, which can be prepared by prolonged heating of the metal, and, among other mercury compounds, the basic sulphate and the nitrate were known to Basil Valentine. As already mentioned, the last-named alchemist occupied himself greatly with the study of antimony, and there are due to him several exact prescriptions for the preparation of butter of antimony (antimony chloride), powder of Algaroth (basic antimony chloride), antimony oxide, potassium antimonate, and antimony sulphide. He does not seem to have been clear as to the composition of these compounds, with the exception of antimony sulphide, about which he at least correctly states that it contains sulphur.

Among the other salts of the heavy metals, we find in Basil Valentine information concerning sugar of lead and green vitriol, which last he obtained by dissolving iron in sulphuric acid, besides some scanty particulars of salts of zinc and bismuth. References to qualitative chemical analysis are also to be found in Basil Valentine. He describes various separations of metals which he carried out by alternate treatment of their solutions with acids and bases, and he employed these methods frequently in practice with success. In this way he succeeded in showing that iron is present in tin and that Hungarian iron contains copper; in copper from Mansfeld he detected silver, and in Hungarian silver he found gold.

Glass Manufacture, Dyeing, etc.

The methods of manufacture of glass and of pottery-ware experienced no improvement worth mentioning in this period ; as the solitary advance in this branch of manufacture may be noticed the employment of glazes containing lead and tin, as well as the burning in of colours.

In dyeing, alum was still in use as a general mordant ; the list of dyes was increased by cochineal and orseille, both imported into Europe from the East. While in antiquity indigo blue found its chief employment as a pigment, we may notice in the course of the alchemistic period an increasingly frequent use of it as a dyestuff.

Organic Compounds.

The knowledge of compounds which belong to the province of organic chemistry experienced only a slight increase. The use of better forms of distillation apparatus, due principally to the Alexandrian school, brought great improvement in the preparation of spirits of wine, and hence greatly furthered the investigation of this compound. The name 'alcohol' is found first in the next period in Libavius, at the end of the sixteenth century ; the alchemists called it *aqua vitæ*. Raymund Lully especially points out the good solvent properties of spirits of wine, and knew besides that it is in most cases rendered impure by admixture of water ; and he showed how to dehydrate it by the aid of fused potassium

carbonate. Basil Valentine mentions its inflammability, and recommends the use of this property for its recognition. The investigations which were carried out with spirits of wine comprised mainly the action upon it of concentrated acids, of hydrochloric acid as well as of sulphuric and nitric acids. The reaction between it and hydrochloric or nitric acid is described by Basil Valentine as the 'sweetening' of spirit. The action of concentrated sulphuric acid on spirit, and the resulting preparation of ether, were also carried out by the alchemists. The formation of alcohol by the process of fermentation, on the other hand, seems to have been unknown to them, for the view was maintained by many that it exists preformed in wine and similar substances. The improvements made in the apparatus for distillation also allowed Geber to separate strong acetic acid by distillation of vinegar, and to prepare by means of it the normal and basic acetates of lead. Besides the distillation of oil of turpentine, a series of ethereal oils were prepared by the alchemists, including oil of rosemary, oil of thyme, etc.

Pharmaceutical Chemistry.

Until towards the close of the alchemistic period pharmaceutical chemistry drew little that was useful from the studies of the alchemists. It was Basil Valentine who applied to the greatest extent chemical preparations to medicinal purposes and so prepared the way for the next period, that of

iatrochemistry. The Arabian physicians, influenced by the endeavour to employ vegetable medicines, brought about the preparation of so-called 'distilled waters.' Apothecaries' shops arose chiefly about this time in Arabia, where they served as places in which the preparation of medicines was carried out strictly according to the prescriptions due to Galen and Andromachus. This system was then introduced through Spain to Germany, and so we find as early as 1474 a pharmacopœia compiled by Ortholf von Baierland.

The preparations which Basil Valentine used in the practice of medicine were mainly those of antimony and mercury. In addition, it was known, even at that time, that it is possible to rub up mercury with fat to make an ointment, and this found various uses in medicine.

CHAPTER III

THE PERIOD OF IATROCHEMISTRY

If one compares the advances which chemistry made in the alchemistic period, treated in the foregoing section, with the great interval of time which it includes, it is not difficult to notice that the two stand in no proportion to one another. The reason for this may be traced to the small interest taken in natural science, by which, as well as an especially strongly developed belief in authority, the Middle Ages, with their ecclesiastical tendencies, are characterized. The reincarnation of the Greek mental tendencies, as it broke forth in the Renaissance, influenced at any rate the development of chemical science. The transition of the Middle Ages to the Renaissance coincides in time with that of alchemy to iatrochemistry. The change which this effected in chemistry expressed itself most prominently in the effort to make it an independent science. Plain signs are to be found of a development of such a kind, but the change did not become complete in this period. Chemistry in the sixteenth and seventeenth centuries stood, on the contrary, under the

influence of a tendency which made it the assistant of another science, and which is distinguished by the endeavour to fuse chemistry with medicine. On this account, the period including the sixteenth and seventeenth centuries is termed that of medicinal chemistry, or iatrochemistry. It should be understood, however, that chemistry, whose repute (as already indicated) has greatly fallen with the growth of alchemistic tendencies, now worked itself up into a generally respected subsidiary science to medicine, and so reached a position from which it was able later to take its place as an independent science.

A turning of the thoughts and views of chemists, such as we have before us in the change from alchemy to iatrochemistry, naturally could not happen in a day. We have found in the preceding chapter, on the one hand, that iatrochemical efforts were being put forth even in the time of Basil Valentine, forming a transition into the new period; and, on the other hand, we have also learnt that alchemistic efforts continued for many years—even, indeed, into our own time. In the main, however, such alchemistic endeavours, proceeding from the standpoint of gold-making, and accompanied by base love of gain and common trickery, were without influence upon the general development of chemical views.

The most decisive influence upon chemical thought in this period proceeded from the physician Paracelsus and his successors, van Helmont and De la Boë Sylvius. Basil Valentine had already put

forward the view that all substances consisted of the three elements sulphur, mercury, and salt, these being regarded after the Aristotelian system as symbolizations of the fundamental properties combustible, volatile, and solid. The iatrochemists generalized this view in such a way that they regarded the human body also as composed of these elements, and sought in the chemical activity of certain constituents of the organism the causes of its functions. The 'life-process,' the physiological phenomenon, was considered as a chemical process in which, in healthy conditions, the active constituents reacted upon one another in the right proportions. That these fundamental substances are present in the right relative quantities is a matter looked after by a being called the *archeus*, which is independent of the human will. 'Illnesses,' the pathological phenomena, are due to a disorganization of the normal chemical process, and are occasioned by an unnatural preponderance of one or other of the constituents. In this way the plague and fever were explained as due to a predominance of sulphur, paralysis and depression to an excessive prevalence of mercury, and diarrhœa and dropsy to a preponderance of salt. Therapeutics then had the task of seeking for chemical means of removing the constituent, excess of which was causing the illness concerned, and so restoring the correct relations necessary to the life-process. Although nowadays these views are open to attack on many points, they were successful in providing the stimulus for a thorough investigation

of chemical processes, and also in giving occasion for the production of a number of new chemical preparations. Along with this there was also united the effort thoroughly to investigate animal substances, in order to discover the active constituents they contained.

Biographical.

We will first mention some of the details of the life of the most important chemist of this period,

Paracelsus.

Philippus Aureolus Paracelsus Theophrastus Bombastus was born in 1493 at Einsiedeln, in Switzerland, and led a wild and wandering life in Europe, Asia, and Africa until his thirty-second year. His enormous mental powers and his gift of sharp observation he turned to account during these wanderings in a striking manner, so that he possessed extensive knowledge of chemical operations when he returned to his native country in 1525. How sharp his observation and how great his powers of comprehension must have been is best shown by his own statement that from his twentieth to his thirtieth year he did not look into any book. A number of fortunate cures led to his appointment as Professor of Medicine at the University of Basle. But not for long did a place of quiet activity there content him. His spirit of opposition, rising to madness, and his efforts to drag to the dust everything in his path, as he did notably with the teachings of Galen and Avicenna, made him a great number of enemies.

Against them, however, he raised himself a crowd of followers by his efforts to popularize science. Finally, however, he sued a canon, who would not pay the sum required of him for a cure, before the magistrate of Basle ; and the latter, with whom he was continually in enmity, sided with the canon, so that he was compelled in 1527 to leave the town. He then recommenced the wild life of wandering of his youth, and lived in turn in Alsace, Bavaria, Austria, and Switzerland. He died in 1541, in the deepest straits of poverty, at Salzburg. In spite of his wandering life, he left numerous writings in various languages, whose contents were vigorously attacked by the old school of medicine. In style and composition he takes a very low place ; his works are often written in a manner quite unworthy of an educated man. They are swollen with a boundless self-conceit, and reflect in every way his changeful life. The controversy over the views of Paracelsus was continued acrimoniously after his death. The most prominent of his enemies was the Swiss physician Erastus—in German 'Lieber'—who fought for the doctrines of Galen against Paracelsus, and of his followers Leonhard Thurneisser seems to deserve mention as the best known, although chemistry does not owe to him any essential advances.

Later we find a series of important chemists who, though working in the direction of the Paracelsian views, recognized the errors they contained, and busied themselves with the endeavour to remove

them as far as possible. They all strove for a rational use of chemical preparations in addition to the drugs of Galen, and in their preparation they brought extensive increase to chemical knowledge.

Turquet de Mayerne was born at Geneva in 1573. He at first lived at Paris as a physician, but was obliged to emigrate to England because, against the opinion of the Parisian doctors, he declared antimony preparations to be indispensable medicines. He was body-physician to King James I. until his death.

Andreas Libavius, also a physician, commanded an extensive knowledge of chemistry, and by reason of his sound general education could give due value to the influence of chemistry upon medicine. He opposed energetically the fantasies of Paracelsus; pointed out also, however, the good ideas of the latter; and so took up an intermediate position between Paracelsus and his opponents. Although he revealed a sound opinion in this matter, yet he was not able completely to break away from alchemistic ideas. To him are due, besides other works, a chemical text-book, which appeared in 1595 under the title *Alchymie.* He died in 1616 as Director of the *Gymnasium* at Coburg.

Van Helmont, who was born at Brussels in 1577, and died there in 1644, studied first philosophy and theology, but soon turned from these studies unsatisfied, and took to medicine. With him, as with Libavius, it is to be noticed that, in spite of his

strikingly sharp and sober powers of observation, he could never free himself completely from alchemistic views. These contradictions are even more remarkable in him than in Libavius, so that it is really scarcely imaginable that the same man whose exact observations on the gases call forth our astonishment should still at the same time share the view that a transmutation of the metals was possible. The collected works of van Helmont were published by his son under the title *Ortus Medicinæ vel Opera et Opuscula Omnia.* He was, in sharpest contrast to Paracelsus, the type of a learned man working in peace ; and hence, although he received many flattering invitations from various Princes, he preferred for love of his scientific occupations to investigate the secrets of Nature in his own laboratory at Brussels.

His most important contemporaries were the two physicians **Angelus Sala** and **Daniel Sennert**. The former lived in the first half of the seventeenth century as body-physician at the Court of Mecklenburg, and the latter was professor at Wittenberg in the first third of the seventeenth century.

Franz de la Boë Sylvius, born at Hanau in 1614, was at first a physician, and later professor, at Leyden. Only the smallest part of the work of this chemist lies in the province of pure chemistry ; he was more engaged in the endeavour to explain as chemical processes the workings of the human body. He contributed much to the extension of chemical

knowledge by the introduction of a series of new preparations into medicine. He died at Leyden in 1672.

Otto Tachenius, a pupil of the preceding, was born at Herford, in Westphalia. Until the middle of the seventeenth century he lived an unsettled, wandering life as an apothecary's assistant, turned in Italy to the study of medicine, and lived in Venice as a physician. It is especially worthy of mention that we find in him the definition of a 'salt' as the compound of acids and alkalis. With great acuteness he perceived how to employ certain reactions for the recognition of substances, and by systematically proceeding in this way assisted the beginning of qualitative analysis. Besides these observations of a qualitative nature, we find in his work also occasionally some dealing with the quantitative examination of chemical processes. He observed, for instance, the increase of weight accompanying the transformation of lead into red lead, but did not perceive how to make use of these observations in any way.

All the chemists named above stood entirely upon iatrochemical ground, and considered chemistry purely as an assistant science to medicine. We find, however, besides, three learned men of that time who went out more from the idea of making their chemical knowledge of use in trade and industry. These three are Georg Agricola, Bernhard Palissy, and Johann Rudolf Glauber.

Georg Agricola was born at Glauchau in 1494; he is therefore a contemporary of Paracelsus. In later years we find him a respected physician at Chemnitz, where he also filled the office of mayor. He practised medicine only by the way, for his chief occupation was the study of mineralogy and metallurgy, his attention being very likely turned to that subject by the mining and smelting industries of Saxony. His writings, in which he gave a series of practical directions for performing chemical operations, stand in the sharpest contrast to those of his contemporary Paracelsus. We find in them a striking clearness of expression, a steady comprehension of the processes described, and an exact indication of the apparatus required for the various chemical processes. But, like most of the chemists of that time, he still, in spite of his mental ability, lay in the power of alchemistic ideas. He died in 1555.

Bernhard Palissy lived in the sixteenth century. Along with Agricola, he was one of the chief exponents of experimental chemistry at that time. He assisted the development of the ceramic industry especially in a marked degree. From a simple potter, wanting in all higher education, he was able to make himself a man of considerable chemical knowledge. His many experiments, continued often with mistaken ideas but with untiring zeal, designed to introduce improvements into his trade, show him as a man free from prejudices and of a determined character. In his opinion, experiment takes the

foremost place, and all speculations made without its aid are to be rejected.

Johann Rudolf Glauber, born in 1604 at Amsterdam, where he died in 1668, possesses many similarities to Paracelsus. His life was very troubled, and his writings are often expressive of great discontent. In many places he showed a great tendency to fantastic and superstitious ideas, and sometimes also he did not shrink from alchemistic trickery. On the other hand, we find in him a good deal of comprehension of chemical processes ; for instance, he first drew attention to the doctrine of chemical affinity, without, however, employing that expression. He sought to explain the decomposition of saltpetre and of common salt by sulphuric acid by saying that one constituent possessed a greater affinity to the other, or, as he put it, 'loved it,' and also 'was loved by it.' He also mentions the first case of a double selective affinity, the double decomposition between mercuric chloride and antimony sulphide, and explains it (at least, from his point of view) correctly.

The Gases and Water.

In describing the life of van Helmont, mention has been made of his successful study of gases. We find in him, indeed, the name 'gas' used for the first time. Before him J. Rey (1630) had described air as a heavy substance, finding that a balloon filled with air increased in weight when more air was

pumped into it, and conversely decreased in weight when it was warmed, and so had air driven out of it. Van Helmont endeavoured accurately to distinguish the various gases, but as he could think of no means by which to collect them for further investigation, his statements are all very vague. He certainly does distinguish, on the one hand, air, gas, and vapour, and on the other hand he speaks of *gas silvestre*, *gas pinguis*, *gas siccum*, or *gas puliginosum*, but what he really understood by these is not very clear. His most exact knowledge seems to have been of carbon dioxide, for he recognized its formation in fermentation and in the combustion of coal, and he also discovered it in the mineral waters of Spa, and knew how to prepare it by treating limestone with vinegar or potassium carbonate with sulphuric acid. Among other gases, we also find mention in the course of the seventeenth century of ammonia. Basil Valentine, indeed, had already acted upon sal ammoniac with quicklime, but says nothing of the gas given off in the reaction; Glauber used it, however, in a series of reactions.

Although the views of the iatrochemists as to the formation of water and its composition were less fanciful than those of the alchemists, yet they do not show any essential difference from them. Many experiments were carried out to investigate the transformation of water into earth, but they did not lead to anything specially worthy of mention.

THE METALS.

Concerning the metals, it is to be mentioned that in this period there may be noticed advances of many kinds, in particular in the simplification of the processes of extraction and purification. Agricola and Libavius endeavoured to carry out at least approximate estimations of the amount of metal contained in the various ores. The chemical preparations which were used in medicine were chiefly metallic salts, and a considerable share in the extension of the knowledge of this class of substances is to be ascribed to this circumstance.

Concerning the metal zinc, whose alloy with copper was known to the ancients, the statements even of this period are still very confused. The name 'zinc' is mentioned in various places in the writings of Paracelsus, Agricola, and others, but there is no accurate information as to what these chemists understood by the term. It rather seems as though they indicated by this name zinc ore in general. Of its compounds, Libavius was acquainted with the oxide, and it did not escape his sharp observation that on heating it a change of colour occurred. Zinc sulphate is often mentioned during this period under the name *Galizenstein*, but its composition was not known. Zinc blende was described by Agricola, not as a zinc ore, but as a useless ore of lead, probably so named because it deceived those who wished to obtain lead from it (Ger., *blenden*, to deceive). Glauber obtained zinc chloride as a thick *oleum* by

digesting calamine with concentrated hydrochloric acid. He was quite aware of its hygroscopic properties, and explains them according to his usual opinions by saying that it must be protected from access of air, because otherwise 'it attracts much air to itself and becomes water.'

Among the compounds of tin, Libavius mentions stannic chloride as a fuming liquid, which he obtained by distilling tin amalgam with mercuric chloride; it bore the name *spiritus fumans Libavii.*

Among lead compounds, Libavius was acquainted with lead nitrate, which he prepared by dissolving lead in nitric acid; and Glauber precipitated lead chloride from such a solution by addition of hydrochloric acid. The knowledge of the other lead compounds, such as lead oxide, white lead, lead sulphide, etc., underwent no change. In the case of iron, also, the opinions remained pretty much the same as in earlier times; steel, which was already known to the ancients, was merely considered to be a specially pure iron. Agricola knew of the varying brittleness of iron, and termed it cold- and red-short. Paracelsus showed how iron might be recognized by means of the sap of galls, and made use of this reaction particularly in the case of mineral waters. Basil Valentine, and after him Libavius, give a series of methods of preparation for iron oxide; those of heating the metal and of solution of iron in vinegar, with subsequent calcination, are quoted as the most important. Ferric chloride was obtained by Glauber by dissolving iron in hydro-

chloric acid as a red mass which liquefied in air; he generally used it in aqueous solution. On allowing the red mass to stand in contact with potassium silicate, he observed a tree-like formation, which was called 'Glauber's iron-tree.'

Among copper salts, copper sulphate, which had long been known, and was obtained in earlier times from mineral waters, was prepared by van Helmont by strongly heating copper with sulphur, and then treating with rain-water; and Glauber obtained it by boiling copper with sulphuric acid. How far from thoroughly individual compounds were sometimes investigated may be noticed again in the fact that Agricola drew no essential distinction between copper vitriol, alum, and iron vitriol. Copper ammonium sulphate was prepared by one Stisser at Helmstedt (1693) by treating blue vitriol with ammonia. That copper can be precipitated by iron is mentioned by Basil Valentine, but this process was regarded by most chemists as a transformation of the metals, although van Helmont and Angelus Sala expressed the correct opinion that copper must exist beforehand in the solutions from which it can be separated by iron.

Concerning the origin and nature of mercury, the alchemistic views were still prevalent; various new processes for its artificial preparation were also tried (*cf.* p. 58). Basil Valentine, for instance, used mercury prepared from corrosive sublimate and lime, and later we find other prescriptions also, though most of them involve wrong ideas. Mercury sul-

phate was employed by the Paracelsian school in medicine under the name of 'mineral turpeth.' In later chemists, however, this name is found also for other mercury preparations—*e.g.*, for mercuric oxide; and Libavius even applies the term 'turpeth' to all those substances which are not prepared by precipitation, but are obtained by evaporation of the solvent and subsequent washing. Mercurous chloride was in early times probably mixed with corrosive sublimate, for the statements as to the relative quantities for the preparation of the former are subject to extraordinarily great variations. The first exact method of preparation for the substance is described by Oswald Croll and Beguin, according to whom a mixture of sublimate, mercury, and red calcined iron is subjected to sublimation. Mercurous chloride was used in medicine under the names *drago mitigatus*, *mana metallorum*, and *mercurius dulcis.* A so-called precipitate prepared from mercuric chloride and sal ammoniac was used by the iatrochemists as salt of Alembroth.

During the alchemistic period the separation of gold and silver by means of nitric acid was invented; to this method there was added in this period that by means of sulphuric acid, which was introduced by Agricola. From all appearances, Glauber also knew how to separate gold from solution; what reagent he used for this purpose is not mentioned. Fulminating gold was the object of various thorough investigations; it was prepared from gold chloride solution, and it was also known that the

presence of ammonium chloride is a necessary condition for its formation, and that none is obtained if potassium chloride is added to this solution instead of sal ammoniac, before precipitating with potassium tartrate. In addition, the chemists of that time knew the property which fulminating gold possesses of losing its power to detonate when it is mixed with sulphur and then this latter burnt off. In Libavius and Glauber there are also statements according to which gold was used for colouring glass red.

Acids, Bases, and Salts.

The conception of acids became more exact in the course of this period. Glauber and Tachenius speak of the different strengths of acids, and mention that a weak acid can be expelled by a stronger, so that, for instance, hydrochloric and nitric acids may be set free by sulphuric acid from substances which contain them. The use of the term *spiritus* for acids was maintained in this period. Concerning their constitution, Sylvius makes some statements in which he advances the view that corrosiveness and sharpness in them, as in the alkalis, depends upon their containing firestuff.

In van Helmont we meet for the first time with the term 'alkali'; he speaks of *alkali fixum*, *alkali volatile*, etc. The opinions as to their constitution have been mentioned above, and since the caustic alkalis were prepared by boiling soda or potash with slaked lime, this view of Sylvius that they contained fire-

stuff found pretty general recognition at that time. An especially obvious reason for this supposition was offered by the lime itself, which takes up firestuff during its burning, and on slaking gives it up again, which was understood by Sylvius as showing that the firestuff was set free by water. Van Helmont went further, and maintained that the lime during burning took up an acid—perhaps sulphuric acid—and this caused the heating of the water on slaking. Various characteristics for recognizing alkalis are given — for instance, their effervescence when treated with acids, and especially the disappearance of the characteristic properties of acids when they are mixed with alkalis.

As distinguished from *sal alkali* as the designation of the alkalis and *sal acidum* as that of acids, the salts bore partly the name 'middle salts,' partly that of *sal salinus*, and to these was added towards the end of the seventeenth century the term *sal neutrale*. Although quite at the beginning of this period it was well known that the middle salts arise from acids and bases, there are yet no indications in the writings of the chemists of the time that they supposed these substances to be contained in them. Not till van Helmont does the view appear that the metal is contained in the salt as such, and in unchanged form. Glauber also held this opinion, and expresses it plainly when he terms butter of antimony a compound of metallic antimony and hydrochloric acid, and calls it '*spiritus salis* in which the *regulus antimonii* is dissolved.'

Glass Manufacture, Dyeing, etc.

The manufacture of glass made not inconsiderable advances in this period, especially in Upper Italy; in Venice the production of coloured glasses was eagerly prosecuted. There exists even a book, *De Arte Vitraria*, published in 1640 by a Florentine named Antonio Neri, in which his wide experience of glass manufacture is preserved to us. As well as the zealously pursued imitation of precious stones, there may be especially mentioned the discovery of a Saxon glass-blower, named Christoph Schürer, of the preparation of a beautiful blue-coloured glass by adding ores containing cobalt to the melt. This glass was termed 'smalt' in commerce.

The ceramic industry owes to Palissy, who has been mentioned above, various improvements in the preparation of beautiful and durable glazes or enamels upon earthenware vessels.

The advances in dyeing consist mainly in the discovery of improved methods for mordanting with alum and iron, and for the fixing of dyestuffs on the material by means of tin solutions. In the list of dyes in use no great increase occurs, in spite of the fact that the discovery of America fell in this period.

Organic Compounds.

The endeavour to refer the activity of the human and animal organisms to chemical reactions soon led chemists on (as has been mentioned at the beginning of this chapter) to the investigation of the indi-

vidual products of the animal body, and even organic substances in general. The result of this was that the number of these compounds experienced a considerable increase, although the knowledge of their composition still remained extremely incomplete.

Acetic acid, which had long been known, the iatrochemists learnt to prepare in pure condition by distillation of verdigris ; Glauber further pointed out that the distillate from wood contained a substance similar to vinegar. Of salts of acetic acid, those of lead were particularly well known, and both the basic and normal acetates were employed.

Although free tartaric acid was not discovered till a much later date, various salts of it were known to the iatrochemists. Potassium tartrate, called *tartarus*, was an important substance at this time ; potassium sodium tartrate was also known, and Mynsicht and Glauber showed how tartar emetic might be made from antimony oxide and potassium tartrate. A distillate from potassium tartrate, which contained pyrotartaric acid, was used by Paracelsus as *spiritus tartari*. The name 'tartar' was often used as a collective name for the salts of vegetable acids, so that one finds that potassium oxalate, called 'salt of sorrel,' is often meant by the term 'tartar.' By the distillation of amber, Libavius and Croll obtained succinic acid. From the sap of sour apples and other fruits salts of malic acid —for instance, the iron salt—were prepared ; the free acid itself was, however, not yet isolated. The

French physician Blaise de Vigenère, towards the end of the sixteenth century, discovered benzoic acid by sublimation of gum benzoin, and for its preparation there exist accurate prescriptions by Turquet de Mayerne. Paracelsus prepared extracts containing tannic acid from galls and from oak-bark, and used them, among other purposes, for the recognition of iron. No statement is made, however, as to the preparation of free tannic acid. Spirits of wine were used by Paracelsus extensively for the preparation of essences and tinctures ; he also probably employed as a drug the mixture of alcohol and ether, still used under the name of 'Hoffmann's drops.' The knowledge of the preparation of ether from alcohol and sulphuric acid soon became forgotten again, and in the knowledge of the compound ethers observed by Paracelsus there is also no considerable advance to be noticed.

Pharmaceutical Chemistry.

As a result of the whole tendency of this period pharmaceutical chemistry developed in the course of it to a marked extent. By reason of the eager search for new chemical preparations capable of employment as medicines, the apothecaries busied themselves more and more with chemical reactions, so that in their shops were reared the most important chemists of the following period. We shall find this in the next chapter in the case of Kunkel, Marggraf, Geoffroy, and especially Scheele. Of inorganic com-

pounds the salts in particular found general employment in medicine ; potassium nitrate, potassium sulphate, and potassium chloride were used under various names ; sodium sulphate, which was obtained by Glauber from the residue in the preparation of hydrochloric acid, and was called *sal mirabile Glauberi*, enjoyed great repute among the physicians of the time. Among ammonium salts, sal ammoniac and ammonium carbonate were employed, as well as ammonium sulphate and ammonium nitrate, discovered by Libavius and Glauber. Ammonium acetate was discovered by the physician Raymund Minderer, and its aqueous solution was used under the name *spiritus Mindereri* as a medicine. Especially prized drugs were the preparations of antimony prepared and introduced by Basil Valentine. By degrees, however, much mischief was done with them, so that strict prohibitions were issued against their use ; they were brought into acceptance again later by the efforts of Sylvius. There found medicinal use chiefly *kermes minerale*, the 'sulfaurat,' and 'powder of Algaroth.' The preparation termed *arsenicum fixum* by Paracelsus seems to have been white arsenic. Bismuth preparations were also dealt with by the apothecaries, the basic nitrate being used, for instance, though mainly as a valued cosmetic. By the influence of Paracelsus and his followers, the use of mercury and its compounds came into great favour ; they administered metallic mercury in a fine state of division in pills, as well as various salts, such as corrosive sublimate, and the

basic carbonate and sulphate, both these going by the name of 'mineral turpeth.' But other chemists also increased the number of medicinal preparations of mercury, calomel and *sal alembroth* being prepared and used at this time, and all these circumstances considerably advanced the chemical knowledge of mercury and its compounds. Sala introduced into medicine silver nitrate, as 'hell-stone' (*lapis infernalis*), in addition to the salts, silver sulphate and silver chloride, formerly known.

In the description of the advances of organic chemistry we have seen that acetic and tartaric acids, as well as various salts of these acids, were prepared. They were all employed in medicine, and were introduced into the apothecaries' shops. Especial mention may be made of sugar of lead, tartar emetic, and sodium potassium tartrate. The distillation product from potassium tartrate, termed by Paracelsus *spiritus tartari*, which has been mentioned above, also found employment in medicine. By the action of the juice of sour apples or other fruits upon metals, various drugs were prepared —for instance, from iron the *tinctura martis pomata*, which is still employed. The ether obtained by the action of sulphuric acid from alcohol was sometimes used as a medicine under the name *oleum vitrioli dulce verum*, but was so soon forgotten that it was at a later date even unknown to such an able chemist as Stahl. It can be plainly seen what a great increase took place in this period in the number of chemical preparations used as drugs, with simul-

taneous abandonment of the vegetable extracts formerly employed, without reference to their chemical composition.

On the whole, then, the joint labours of chemistry and medicine were very fruitful, and increased chemical knowledge very considerably in many directions. By this means, also, the general comprehension of, and interest in, chemical processes was advanced in the way which was necessary to introduce the further development beginning in the next period.

CHAPTER IV

THE PERIOD OF PHLOGISTIC CHEMISTRY

DURING the period of iatrochemistry described in the preceding chapter chemistry made its way to the position of a respected assistant of medicine; in the present period it went a step further, and made for itself an independent position among the sciences. For this reason it became possible to increase chemical knowledge in the most extensive manner, and to evolve the desire of seeking after truth independently. This could not happen so long as chemistry was still a mere assistant to other forms of training, for under those conditions the direction of its labours must necessarily be more or less one-sided.

Henceforth the object of chemistry was fixed: it was occupied with the knowledge of the constitution and decomposition of substances, with the investigation of the phenomena observed in these combinations and decompositions, with the laws according to which these processes occur, and with the determination of how far the properties of substances depend upon their composition.

The Theory of Phlogiston.

The investigations which chiefly occupied the chemists of this period were directed to the investigation of the nature of combustion, and they led to the establishment of the phlogistic theory, with which we shall be more particularly concerned below. As this theory formed the leading idea from the beginning of the eighteenth century to the great researches of Lavoisier on oxygen in 1775, that interval of time bears the name of the Phlogistic Period. The investigations themselves were in general only carried out qualitatively, for only under these conditions was the phlogistic theory capable of existence ; it fell to pieces as soon as the method of exact quantitative investigation was introduced by Lavoisier.

Of a date much older than this time is the opinion that combustion caused a destruction or a decomposition of the burning substance, that in combustion something which appears to us as flame separates from the burning substance, while the residue represents the other constituent of the substance. The effort to ascribe to sulphur the principle of combustibility led Sylvius at the end of the iatro chemical period to maintain that sulphuric acid, which forms the combustion-product of sulphur, is contained in combustible substances. Kunkel regarded this as generally true ; Boyle thought it certainly probable, but by no means proved : he compares, indeed, combustion with the acidification of

sulphur, but supposes the combustible principle to be a 'combustible earth.'

To Stahl is due the most precise expression of the views regarding combustion which brought together, as one and the same phenomenon, the changes experienced by all substances under the action of fire. He makes this property of combustibility dependent upon a constituent common to all combustible substances, which he names 'phlogiston.' The more easily a substance shows the phenomenon of combustion and the greater the flame, the more phlogiston does it contain. According to this, coal is to be regarded as a substance which is distinguished by especial richness in phlogiston. The fact that an acid is formed in the combustion of sulphur or phosphorus led to the view that these two substances were compounds of the acid concerned with phlogiston. If this view is extended to the metals and the oxides obtained by heating them, the metals are to be regarded as compounds of the oxides with phlogiston. Stahl accordingly explains the reduction of the oxides to metals by saying that in this reaction phlogiston transfers itself from a substance which is rich in it to one that contains less ; so that when a metallic oxide is reduced with coal the latter gives up phlogiston to the oxide, which can then combine with it to form the metal. It scarcely needs to be emphasized that Stahl's theory of combustion is about the exact opposite to what we now understand by combustion.

Of the advances which chemistry made during

this period, the more precise definition of the idea of an 'element' by Boyle deserves especial mention. Boyle applies this term to the constituents of compound substances which can really be prepared, but cannot be further decomposed. With this definition the possibility, of course, always remains open that we may some day succeed in decomposing further a substance hitherto regarded as an element. On the whole, however, Boyle's definition of an element coincides with that now in use.

It is remarkable, however, that chemists of repute, including even Stahl, could not free themselves in many matters from alchemistic ideas; one even finds sometimes an inclination towards the Aristotelian doctrine.

Biographical.

In spite of the fact that the phlogistic period was comparatively short—for it does not even comprise a whole century—it was nevertheless rich in important chemists, of whom Boyle, Becher, Cavendish, Priestley, and Scheele are the most prominent.

Robert Boyle was born in 1627 at Youghall, county Cork. In his youth he travelled through France, Switzerland, and Italy, passing two years at Geneva, where he pursued his first chemical studies. In the year 1654 he moved to Oxford; after 1668 he lived in London as President of the Royal Society, and he died there in 1691. His nobility and modesty of character, so opposed to external

display, when compared with the almost shameless vanity of a Paracelsus, present a contrast scarcely to be paralleled. His services in the development of chemistry were chiefly in the direction of the investigation of the gases ; it was he who first expressed the law of the simple relation between pressure and volume in gases ($p \times v =$ constant). Applied chemistry also, especially the analysis of chemical compounds and pharmaceutical chemistry, owes to him, as we shall see later, considerable extensions. Boyle left many writings, which give us pleasure by their simple style and clearness of expression ; they stand in the closest relation with his character, and in the sharpest contrast to the mystic modes of expression of the alchemists.

Nikolaus Lemery, who was born in 1645 and died in 1715, followed Boyle closely in his theoretical views ; his chief contribution to the advance of chemistry was his endeavour to make it as generally accessible as possible ; and to this end his *Cours de Chymie*, published in 1675, contributed not a little. For a long time this work was the best text-book of chemistry, as is strikingly proved by the fact that thirteen editions of it appeared during Lemery's lifetime.

Johann Kunkel was born in 1630 at Rendsburg. He was at first an apothecary, and later took to alchemy. Although he was fully convinced of the possibility of the transmutation of the metals, his honest character is repeatedly evidenced by his

various exposures of the trickery of his alchemistic contemporaries. He led a troubled life as alchemist in the service of various Princes, and died at Stockholm in 1702. His chief services to the science were the advancement of experimental chemistry and practical chemical knowledge in general.

Johann Joachim Becher, born at Speyer in 1635, sought in theoretical questions to revive the views of Basil Valentine and Paracelsus ; in other respects he was, like Kunkel, an alchemist, and practised as such at various European Courts, such as Mayence, Munich, and Vienna. His views on combustion, on which Stahl's phlogistic theory was mainly founded, have already been mentioned at the beginning of this chapter.

Georg Ernst Stahl, born at Ansbach in 1660, devoted himself at first to the study of medicine ; in 1693 he was called to the professorship of medicine and chemistry at Halle. His occupation with chemistry sprang solely, as all his works show, from an eager desire to investigate the truth. Although his theory of phlogiston was built, in default of quantitative investigation, upon completely false ideas, yet his sharp powers of observation (which were necessary in order to treat this theory as generally as possible) contributed much to the advancement of chemical knowledge. In the year 1716 he became body-physician to the King of Prussia at Berlin, and he lived there till his death in 1734. Several of the most important chemists

of this time proceeded from his school; as such may be named Black, Cavendish, Marggraf, Scheele, Bergmann, and Priestley.

Friedrich Hoffmann was born at Halle in the same year as Stahl—1660. He studied medicine, mathematics, and natural science in his native town, and was afterwards Professor of Medicine at the University there. He fought the erroneous views of the iatrochemists Sylvius and Tachenius with particular success. In the main his work benefited medicine, and pharmaceutical and analytical chemistry. Although his ideas upon combustion followed those of Stahl, his opinions on the reduction of the metallic oxides differ considerably from Stahl's, approximating more to those held at the present day. For a time he worked in Berlin, but died in his native town in 1742.

Hermann Boerhave, who was born at Voorhout, near Leyden, in 1668, and died at Leyden in 1738, studied at first theology, but soon turned to medicine, and occupied himself particularly with chemistry. In 1709 he became Professor of Medicine, Botany, and Chemistry at Leyden. We possess a large text-book of his, *Elementa Chemiæ,* which appeared in 1732. In his case also we find, as in that of his contemporary Hoffmann, views upon the metallic oxides which differ from those of Stahl.

The last well-known chemist to maintain the phlogistic system in Germany was **Andreas Sigismund Marggraf** who was born in 1709 and died

in 1782. At first an apothecary, he soon gained wide chemical knowledge by zealous study at the *Hochschulen* of Frankfurt on the Oder, Strassburg, and Halle, and at the Freiberg School of Mines. He accepted completely the views of his teacher Stahl, and could not free himself from them, although he observed himself, in his investigations on phosphoric acid, that the transformation of phosphorus into phosphoric acid is accompanied by an increase in weight. He also carried out extensive investigations on the sap of the beetroot, and succeeded in proving the presence of sugar in it.

Besides these German phlogisticians there were also some of French, English, and Swedish nationalities.

Stephen Francis Geoffroy the elder, born in Paris in 1672, was the son of an apothecary, and studied chemistry and medicine. In 1712 he became Professor of Medicine at the Jardin des Plantes in Paris, and died in the year 1751. His investigations mainly concerned the doctrine of chemical affinity; their results were put together in his *Tables des Rapports*.

His pupil, **Duhamel de Monceau,** who was born in 1700 and died in 1781, occupied himself deeply with the application of chemistry to agriculture and manufacture. His investigations also furthered the advance of pure chemistry; for instance, he was the first to prove the difference between caustic soda and caustic potash. He pre-

pared the former from common salt, and found it to be the base of common salt, borax, Glauber's salt, and soda. The first proposals for the artificial preparation of soda from sodium chloride are also due to him.

John Francis Rouelle (1703-1770) was active during this period chiefly as a teacher of chemistry. Lavoisier and Proust were among his pupils. He is distinguished by his sharp powers of observation, which enabled him to define the idea of a 'salt' (p. 88). His papers on this subject were published in 1745 in the *Mémoires de l'Académie Française.* Another teacher of this period at the Jardin des Plantes was **Peter Joseph Macquer**, and various text-books are due to him. His other work is more related to applied chemistry, especially to the improvement of the porcelain manufacture and of dyeing.

Joseph Black, born in 1728, was Professor first at Glasgow and later at Edinburgh. His various experiments upon carbon dioxide and its compounds with the alkalis and alkaline earths are marked by the greatest acuteness. Physics also owes to him the discovery of 'latent heat.' As Black always paid great attention to quantitative investigations, it is easy to understand that when the discovery of oxygen had furnished the correct explanation of combustion he gave up his phlogistic views and adopted the doctrine of Lavoisier. He died in the year 1799.

Henry Cavendish, born at Nizza in 1731, devoted himself mainly to physical and chemical research. He was the discoverer of hydrogen, which he called 'inflammable air.' He proved that water is composed of hydrogen and oxygen, and that air is a mixture of nitrogen and oxygen of constant composition, and he also showed that nitric acid is formed by the combination of these two gases. Although he contributed so much by these investigations to the fall of the phlogistic theory, he himself could not decide to change his views in this connexion; he contended against Lavoisier's theory of combustion until his death in London in 1810.

Joseph Priestley, born at Fieldhead, near Leeds, in 1733, led, unlike Black and Cavendish, an unsettled life, full of vicissitudes and persecution. This was due as much to his personal intolerance as to his peculiar attitude towards the Church, for, a theologian by profession, he dealt with scientific questions in his preaching. His work contributed greatly to the advance in the knowledge of the gases. In 1774 he discovered oxygen, although his beautiful experiments with this gas did not lead him to a correct understanding of the process of combustion; on the contrary, he was, till his death in 1804, one of the most zealous supporters of the phlogistic theory. This is the more difficult to comprehend, since he describes the circulation of oxygen in the organic world through the metabolism of animals and plants in the correct manner.

Torbern Bergmann, professor of physics, mineralogy, and chemistry, was born in 1735 at Katherinenburg in West Gothland. His most important services to chemistry lay in the domain of analysis, the systematic treatment of which he extended by important new methods. Bergmann also brought the views upon chemical affinity to a greater clearness than had obtained before his time. Excessive work with a naturally weak constitution caused his death at the age of only forty-nine.

Carl Wilhelm Scheele, one of the most distinguished chemists of all times, was born in 1742 at Stralsund, which then belonged to Sweden. At the age of fourteen he began his career as an apothecary, and practised that calling at Gothenburg, Malmoe, and Stockholm. In the peace of his apothecary's shop at Köping, Scheele discovered successively chlorine, oxygen, and baryta. Unfortunately he also could not shake himself free from the bonds of the phlogistic theory, and so it happened that although he was incomparable in observation and comprehension of facts, he often met with misfortune in working out their meaning. Among his other work may be mentioned his investigations of manganese dioxide, and of the formation of potassium nitrite and oxygen when saltpetre is heated. He died in 1786 at the age of forty-four.

THE GASES.

In the knowledge of gases, which was considerably extended by the researches of van Helmont in the preceding period, a considerable advance is also to be noted in this period. In the accounts of the lives of the individual chemists of the time references have already been made to the discovery of various gases—*e.g.*, oxygen, hydrogen, etc. Even before their discovery one sometimes finds the view appearing that the air is a mixture of two gases, and the researches upon the respiration of men and animals led also to a sharp distinction between atmospheric air and the gas now known as carbon dioxide, which was then termed ' poisoned air ' or ' fixed air.' Complete clearness in this connexion was brought by the discovery of oxygen, which was isolated by Priestley on August 1, 1774, and also independently, by another method, by Scheele about the same time. Priestley prepared it first by heating mercuric oxide, and afterwards also, as a check upon his experiments, by heating red lead. He recognized oxygen as a gas not absorbed by water, and capable of supporting extraordinarily vigorous combustion. Scheele's starting-point for the preparation of oxygen was black oxide of manganese, which he heated with phosphoric or sulphuric acid. He also found that the gas evolved on heating saltpetre is identical with that obtained from manganese dioxide. The further investigations which he carried out with this gas soon led to its recognition

as the substance which was the active principle in respiration and combustion. Its discoverers, however, did not agree with this view. We have already seen that both Priestley and Scheele were supporters of Stahl's phlogistic theory till their deaths, and so it is not remarkable that they explained the reactions of this gas also in that way. From Priestley it obtained the name of 'dephlogisticated air,' while Scheele called it 'fire-air.'

Carbon dioxide was also subjected to thorough investigation, which resulted, as has been mentioned, in the recognition of its essential difference from atmospheric air. Black first expressed this opinion, and the term 'fixed air' is due to him; he also recognized its formation in the burning of coal, in the fermentation of liquids containing sugar, in the respiration of men and animals, and in the reaction between alkalis (alkaline carbonates) and acids. He further observed its power of giving compounds with caustic alkalis and with lime, a reaction which he compared with the neutralization of the alkalis by an acid. Further contributions to the knowledge of this gas are due to Cavendish, who observed that when it was passed into lime-water it gave a precipitate at first which dissolved if the passage of gas continued. This formation of the compounds which we now term bicarbonates was employed by him for the explanation of a point of great interest at that time—that natural waters dissolve earth, but deposit it again on boiling. The characterization of fixed air as an acid, which

had not been made by Black, is due to Bergmann, who observed that carbon dioxide dissolved in water acted as a solvent upon iron, zinc, and also (as Cavendish had found) upon calcium carbonate. Divergent views prevailed as to the constitution of carbon dioxide ; it was by some regarded as phlogisticated hydrochloric acid, by others as a modification of sulphuric or nitric acid. The opinion which came nearest the truth was that it was a compound of oxygen and phlogiston. In that case, phlogiston would be equivalent to carbon, but the supporters of the phlogistic theory did not succeed in expressing this.

The old and deep-rooted notion that water could be turned into earth or stone still influenced almost the whole of this period. Although various workers expressed a different opinion, they had little chance while men like Boyle and Geoffroy still maintained the possibility of such a transformation. Le Roy considered the earth left behind on the distillation of water to consist of substances dissolved in it ; Scheele investigated this residue more closely, and found in it silica and lime. A change in these views, as also in those of the constitution of water generally, was effected by the discovery of hydrogen by Cavendish. As has been mentioned several times, we find in earlier periods many statements which show that hydrogen had been observed as a gas evolved on solution of iron in acids, but that it was not held to be a particular gas, being partly confused with carbon dioxide and partly regarded as air.

Turquet de Mayerne, and after him Boyle and Lemery, probably knew of its inflammability, and by the believers in phlogiston it was regarded as the phlogiston of the metals, being even sometimes considered identical with phlogiston. It was Cavendish who first showed this gas to be a peculiar kind of air. The accurate investigation which Cavendish carried out upon hydrogen led in the first place to the determination of its specific gravity, which he found to be $\frac{1}{11}$ that of the air (the correct figure being $\frac{1}{14}$). He further examined its power of exploding, and found that this property is not observed in the case of pure hydrogen, but appears as soon as it is mixed with air or oxygen. In 1776 Macquer and De la Methérie observed that a liquid resembling water is formed in the combustion of hydrogen, but they did not consider it to be water, regarding it, indeed, as the acid employed in the generation of the hydrogen. Cavendish, on the contrary, maintained that this liquid was water, and his contention was completely confirmed by Lavoisier's re-examination of the matter. In this way the composition of water was proved, and Lavoisier gave also an analytical proof of it by carrying out its decomposition by passing steam over red-hot iron. The quantitative determination was carried out by the same chemist in 1786; he found water to consist of 22·9 volumes or 13·1 grammes hydrogen, and 12 volumes or 86·9 grammes oxygen. These values are very near to the true composition (24 volumes hydrogen to 12 volumes

oxygen, or 11·11 grammes hydrogen to 88·89 grammes oxygen).

The results of these discoveries, investigations, and observations upon hydrogen and water were, as was of course to be expected, received with great scepticism by the chemists of the time. The notion of the elementary nature of water was, in fact, so deeply rooted that it could not be upset in a short time even by exact analyses. Even Priestley was in the year 1800 still not convinced that water is a compound substance, and still considered the product of the combustion of hydrogen to be nitric acid. As late as 1801 we find Ritter trying to maintain the elementary nature of water, and describing (by reason of the electrolysis of water) oxygen as water with negative, and hydrogen as water with positive, electricity. This view also was vanquished in time by the investigations which Lavoisier had made.

As the views concerning the composition of water became clearer in this period, so also did those concerning air.

In earlier times various opinions were expressed as to the composition of the air, but as it seemed desirable not to mention these in the accounts of those periods we must here go back a little.

Mayow describes very fully the behaviour of air in respiration in his *Tractatus de Respiratione et de Rachitide* (1668) and in the *Tractatus Quinque Medico-physici* (1669), and he comes to the conclusion that not all the air takes part in respiration

and combustion. He further discovered that the air which remains after a combustion is somewhat lighter than common air, that it will not support combustion, and that it is not absorbed by water. He carried out its preparation by conducting the combustion in closed vessels over water, so that of course the carbon dioxide formed was absorbed by the water. Boyle had occupied himself with the investigation of the calcination of metals in closed vessels, but neglected to examine more closely the residual air ; this was repeated in 1710 by Hawkslee, who found that this gas would not support life, and also noticed that it extinguished flames. This kind of air was regarded by Mayow and others (in opposition to Boyle) as 'nitrous,' and the residue after combustion was called 'nitrous air.' In 1772 Rutherford recognized the gas to be a peculiar kind of air, and Priestley, Scheele, and Lavoisier subjected it to thorough investigations. These confirmed Mayow's statements as to its weight and other behaviour. In the course of time various other methods of preparation were discovered : Berthollet in 1791 obtained it by heating animal tissues with nitric acid, while as early as 1788 Fourcroy had found it in the air-bladders of fishes, and had recognized it as a general constituent of all animal substances. Various names were applied to the gas : Mayow and others called it 'nitrous air'; Priestley, in 1775, gave it the name 'phlogisticated air'; Scheele, in 1777, 'mephitic air'; Chaptal, after the discovery of its presence in nitric acid,

proposed the name 'nitrogène'; Fourcroy, after the discovery that ammonia could be obtained from it under certain conditions, suggested 'alcaligène'; Lavoisier called it at first 'mofette atmosphérique,' but later (1787) 'azote,' in order to give prominence to its suffocating properties. The prevailing views as to the constitution of this constituent of the air were very confused. Priestley and most of the followers of the phlogistic theory regarded it as oxygen or air saturated with phlogiston, as indicated by the term 'phlogisticated air.' Cavendish regarded nitrogen as phlogisticated nitric acid, for he found that nitric acid is formed by the union of nitrogen and oxygen. Clear ideas only appear with the opponents of the phlogistic theory, an account of whom will be given in the Second Part.

In the biography of Scheele reference has already been made to the discovery of chlorine by this chemist. His researches on manganese dioxide, which led him to the isolation of oxygen in 1774, gave occasion to this discovery also in the same year. In digesting manganese dioxide with hydrochloric acid, Scheele observed a smell like aqua regia, and therefore collected the gas evolved in this reaction separately. On closer examination he found that it possessed an intense yellow colour, that it destroyed vegetable dyes in such a manner that they could not be restored by the action either of acids or alkalis, that cinnabar (mercuric sulphide) was turned into corrosive sublimate by its action, that it vigorously attacks all metals, including even gold,

and that animals suffocate and flames are extinguished in it. Other observers noticed the solidification of the damp gas when cooled, but it was not discovered till later that the solid substance formed is not chemically identical with the gas. One Westrumb also observed in the year 1789 the incandescence which the metallic sulphides, as well as bismuth, antimony, and other metals, show in an atmosphere of chlorine. The gas was termed in England 'dephlogisticated marine acid' ('marine acid' being the name at that time used for hydrochloric acid). This nomenclature was proposed by Scheele, who supposed that in the reaction between hydrochloric acid and manganese dioxide the phlogiston of the acid was given up to the manganese dioxide, and that the gas evolved was therefore hydrochloric acid (marine acid) minus phlogiston.

Sulphur and its Compounds.

When it had been observed that sulphuric acid arises in the combustion of sulphur, the earlier view which saw in sulphur the principle of combustibility was modified, and it came to be regarded as a compound of sulphuric acid with the combustible principle. Then Stahl set up his theory of phlogiston, and it became obvious that, if this view were taken, sulphur must be considered to be a compound of phlogiston with sulphuric acid. This opinion formed, indeed, one of the mainstays of Stahl's phlogistic theory. What idea Stahl had of

this compound is most clearly shown by the fact that he ascribed to sulphur a constitution analogous to alum or vitriol, regarding it therefore as a kind of phlogiston sulphate. He and his followers were strengthened in this opinion, especially by the frequent and easy formation of sulphur in various chemical processes, as, for instance, in the treatment of concentrated sulphuric acid with oil of turpentine, or in the rotting of wormwood leaves in a solution of sodium sulphate (Glauber's salt) : these observations were made in 1769 by the brothers Gravenhorst at Brunswick. All these phenomena were therefore practically in very good agreement with the phlogistic theory, and so it is not by any means remarkable that Boyle's observation that sulphur might be a constituent of sulphuric acid, and the declaration of Mayow that this really is the case, remained quite unnoticed. A change in these views only occurred when Lavoisier invoked the assistance of the balance. On quantitatively investigating the combustion of sulphur he found that the latter increases in weight, and he correctly ascribed this increase in weight to the circumstance that by the combustion of sulphur a compound with air—that is to say, oxygen—had been formed. To confirm this view he decomposed oil of vitriol by heating it with mercury, and determined the gas evolved to be a mixture of sulphurous acid and oxygen. He was also able to prove that the sulphurous acid consisted of sulphur and oxygen, and that it therefore forms an intermediate substance between

sulphur and sulphuric acid. Sulphurous acid was also regarded by the believers in phlogiston as an intermediate substance between sulphur and sulphuric acid, but according to their ideas the relations were that sulphurous acid was a compound of sulphuric acid with a little phlogiston, and sulphur a similar compound with more phlogiston. Lavoisier's quantitative investigations of the combustion products of sulphur furnished on the principles of his theory of oxygen the proof of the elementary nature of sulphur, and at the same time robbed the phlogistic theory of one of its most important supports.

It was known to the alchemists, as has been mentioned above, that sulphur dissolves in caustic alkalis, and can be precipitated again by acids. The gas, however, which is evolved in this reaction was not paid much attention to, and where mentioned is only referred to as sulphurous vapour. Rather more notice was taken of it in the course of this period, and in particular its various properties were subjected to closer investigation. Its inflammability was discovered by the apothecary Meyer, of Osnabrück, and is described by Rouelle, and in addition various chemists mention its power of forming precipitates with certain metallic solutions. Scheele states that water absorbs it and becomes possessed of its smell, that it deposits sulphur on standing in the air or when nitric acid or chlorine act upon it, and that sulphur and hydrogen are formed when it is strongly heated. He prepared it

from the sulphides of calcium, and also by treating manganese sulphide or ferrous sulphide with sulphuric acid, and he called it ‘air of liver of sulphur.’ Other chemists termed it ‘stinking sulphur-air,’ ‘hepatic air,’ or ‘sulphuretted hydrogen’ (*hydrogène sulfuré*).

The followers of the phlogistic theory supposed this gas to consist of sulphur, phlogiston, and heat; phlogiston in this case is to be considered as identical with hydrogen. How confused the prevailing opinions were on this subject is shown by the fact that sometimes the view is found maintained that sulphur is not directly contained in the gas, but is only carried up with the vapour, so that it may be removed by washing with water. Kirwan even doubted whether it really contained hydrogen.

It did not escape the keen observation of Scheele that when much sulphuric acid was added to a solution of liver of sulphur (potassium sulphide) the gas described above was not obtained, but an oil was precipitated instead; he was not, however, clear as to the constitution of this compound, which is now known as hydrogen persulphide. Carbon disulphide (at least, in the form of vapour) was also obtained by Scheele by heating carbon with sulphur. Its preparation in the liquid state and its accurate investigation do not fall, however, in this period.

PHOSPHORUS.

In the period of transition from that of iatro-chemistry to that of the phlogistic theory occurs also the discovery of phosphorus. It is not clear to whom the honour of its first preparation is really due. One Dr. Brand, of Hamburg, and the chemist Kunkel both described it about the same time, but whether the work of Kunkel was independent of Brand's was a point of contention at an early date. Kunkel himself makes no claim of priority in any of his writings, so that it rather seems as though this was ascribed to him by his pupils. The preparation of phosphorus was carried out, according to the statements of these two workers, by strongly heating a mixture of evaporated urine and sand. In time other modes of preparation were found out, such as those from various plants ; we find accounts of these in Marggraf, who describes its formation from mustard, the seeds of cress, and from wheat. Whether its formation from calcium phosphate, so important for its technical preparation, was discovered by Scheele or by Gahn is also doubtful. In any case, the reaction is first mentioned in Scheele. The term 'phosphorus' (fire-bearer) was given it from its property, naturally very soon noticed, of shining continuously in the dark.

It was also known at an early date that when it is burned in the presence of water an oily product is formed, the acid properties of which were observed by Boyle, and this observation led for a

time to the opinion that it was nothing but sulphuric acid. Stahl considered it, on the contrary, to be a compound of phlogiston and hydrochloric acid, explaining the presence of the latter by the high percentage of common salt in urine.

According to these phlogistic views, phosphorus would be a compound of phlogiston with the acid produced in its combustion; and since this latter consists, according to Stahl, of phlogiston and hydrochloric acid, it follows that phosphorus is a compound of very much phlogiston with a little hydrochloric acid. In fact, one does find the view maintained that an artificial production of phosphorus would be possible by mixing hydrochloric acid and phlogiston in the right proportions.

Acids, Bases, and Salts.

Opinions upon the conception of acids underwent various changes in this period. Boyle defined them by their solvent properties, by their formation of so-called 'middle salts,' and by their power of precipitating sulphur and other substances from solution in alkalis, and of changing vegetable colours or reproducing such as had been changed by alkalis. In the preceding period the view had developed that the different acids were of different strengths, but in 1732 Boerhave supposed, on the contrary, that all acids possess the same strength, and that the apparent difference in this respect between acetic and sulphuric acids was due to a

different content of water in the two substances. This view was founded on the observation that equal quantities of different acids always saturated the same amount of alkali. Hellot, in 1736, divided acids into mineral, vegetable, and animal acids, and so termed hydrochloric acid, sulphuric acid, and nitric acid *acides mineraux*, in contradistinction to formic acid (prepared from ants), which he reckoned among the animal acids. Upon the constitution of the acids Stahl's opinions were more or less dominant during the whole period. As Stahl regarded acids, bases, and middle salts all as salt-like compounds, he saw in the strongest acid the very type of a salt. On this account sulphuric acid represented to him the only fundamental principle of salts, producing the innumerable other saline mixtures of less simple type by combining with various other substances not of a saline character. This mineral acid, however, according to Stahl, was only an elementary substance of the second order, and is itself produced by the combination of elementary water and elementary earth.

Nitric acid he regarded as the primitive acid changed by putrefaction and mixed with phlogiston, while hydrochloric acid was the primitive acid diluted with a mineral principle. As to what conception is to be formed of the primitive acid which these explanations presuppose, no clear idea seems to have prevailed among the chemists of the time. Stahl himself sought for some time to identify it with phosphoric acid, but he afterwards gave up

this opinion. From the nature of the case, this view must also lead to the belief in the possibility of transforming hydrochloric, sulphuric, and nitric acid into one another.

As this notion of a primitive acid lent itself to generalization, Stahl endeavoured to explain the constitution of bases also in this way. He thought to effect this by the supposition that in bases the proportion of primitive acid is very small, being smaller the more alkaline they are. In this way he explained, for instance, that cream of tartar becomes alkaline on treatment with lime because primitive acid is removed from it by the latter. When Boerhave maintains in opposition to this explanation that the caustic properties of lime only proceed from fire, it seems as though he would explain the causticity of potassium bitartrate treated with lime as due to an absorption of fire-stuff. Whether Boerhave really was of this opinion cannot be said with certainty, for his statements on this point are very indefinite; in any case, this explanation would be the exact opposite to Stahl's, for he sought to explain the alkalinity by the loss of a hypothetical substance, while Boerhave ascribed it to the absorption of one. As up to this time chemists had quite neglected the gas evolved on solution of some alkalis in acids, no distinction had hitherto been made between those alkalis which dissolved in acid with effervescence, and those which gave no such effervescence. In the course of this period, however, attention was paid to this difference

of behaviour, and two different opinions were advanced to explain it. One is due to Black, and rests upon exact quantitative investigations, principally executed with lime and magnesia. The other was originated by the apothecary Johann Friedrich Meyer, of Osnabrück (*cf.* p. 80), and is permeated with phlogistic theories. It is, therefore, not remarkable that the latter view found more adherents than that which rested upon Black's exact investigations. The latter was able to prove quantitatively that if he calcined *magnesia alba* in weighed amount, so that it dissolved in alkalis without effervescence, and then precipitated the *magnesia alba* again from this solution with potassium carbonate, its amount agreed with that taken at the beginning. It was also shown in this investigation that when the carbonates of lime and magnesia are calcined, the gas evolved is identical with that evolved when these substances are dissolved in acids. Against this Meyer maintained the view that limestone, when heated, only lost water, and that it took up firestuff from the substances whose combustion was heating it, and that it was this latter which made it caustic. According to him, effervescence with acids is a general property of the alkalis, which they lose on heating simply because they absorb firestuff which is similar to an acid. The firestuff itself Meyer termed *acidum pingue*, a name which was subjected to various changes by other phlogistic chemists. Meyer considered then the caustic alkalis to some extent as salts of alkali and *acidum pingue*, from

which this acid might sometimes be expelled again even by water. In this way was to be explained the heating of quicklime when treated with water, and as this behaviour of lime is not explained by Black's views it also formed a ground for the preference of Meyer's explanation at that time. The increasing importance of quantitative investigations, which even towards the end of this period were continually gaining ground, was more than the theory of Meyer, the whole structure of which was of a purely qualitative nature, could withstand, and Lavoisier's thorough investigations finally decided the controversy which had arisen upon the matter in favour of the adherents of Black's theory.

Hand in hand with these theoretical developments went also an augmentation of the experimental material. In the course of this period several so-called 'earths' were discovered, which from their chemical properties, such as stability towards heat and insolubility in water, were soon seen to be closely related to the alkalis. Marggraf discovered alumina in 1754; Scheele, in 1774, baryta; and by the year 1782, in addition to these, magnesia, lime, and silica were distinguished as simple kinds of earths.

Many chemists occupied themselves with the question as to whether the alkali contained in wood ashes is only formed in the combustion, or is previously present in the wood. The French chemist Bourdeleine sought to show (1727 and 1730) that in wood the alkali is combined with an acid which

is destroyed in the burning, and so the alkali is set free. This view was opposed by Stahl, for he had found that the extract of a certain amount of wood gave more alkali after evaporation and combustion than a similar amount immediately burnt. The explanation of this he believed to be that the constituents of the alkali in wood are too widely separated, and get driven off by the fire separately before they can combine to form the alkali. Marggraf, in 1764, brought valid experimental proof of the pre-existence of alkali in plants. He showed, in fact, that the presence of fixed alkali in a natural vegetable extract obtained without previous combustion, such as tartar or salt of sorrel, could be proved from its yielding saltpetre when treated with nitric acid.

The year 1744 brought a sharper definition of the term 'salt' from Rouelle. Up to that time the principal characteristics for salts had been taste and solubility. The solubility was deemed so important that, for instance, the potassium sulphate which separates at once when oil of vitriol is treated with strong potash was held to be different (on account of its supposed insolubility) from that slowly crystallizing from dilute solutions; indeed, it was not even reckoned among the salts. Rouelle gave the name 'middle salt' to every compound of an acid with a base. In this way he placed with the salts a number of compounds which were not numbered among them according to the prevailing views just described—for instance, calomel and

chloride of lead. Besides this, however, Rouelle divided the various salts into neutral, acid, and basic salts. In the neutral salts the base is just saturated with the acid, in the acid salts there is an excess of acid present, while the basic salts contain less acid than the base requires. Although his papers containing these ideas include many errors, they have, nevertheless, formed the groundwork for our present views upon this matter. One of these errors, for instance, was that in his subdivision into the three groups he was not able to throw aside solubility as a test. On the contrary, he sought to recognize salts by their different solubilities, considering acid salts as the most, and basic salts as the least, soluble. Bergmann bore the chief share in building up Rouelle's conception, and in opposing the objections to it that were brought forward, chiefly by Baumé. After Bergmann there came in the next period Berthollet, who also proved that in the various salts all the constituents are chemically united. Bergmann also successfully combated Stahl's view that only reguline, not calcined, metals could unite with acids to form salts, a process in which phlogiston was, of course, supposed to play a part. To Stahl is due also the term 'double salt,' but it was not used by him in its present sense; it signified the same thing as middle salt. This system led to potassium sulphate being termed a double salt.

In this connexion it remains to be mentioned that, while working at a method for obtaining

potassium carbonate in crystalline form, one Carthäuser, in 1757, discovered the acid carbonates (bicarbonates) of the alkalis.

Chemical Industry.

Into this period also fall the successful endeavours of various chemists, such as Boyle, Kunkel, Marggraf, and Macquer, to apply to industrial ends scientific knowledge of chemical reactions. Here, therefore, we find the beginnings of chemical manufacture. As early as the middle of the eighteenth century a distinction was drawn by chemists between pure chemistry and technical chemistry; this is most plainly shown by the appearance at that time of a series of text-books and manuals upon the various branches of technical chemistry. The successful rise of chemical manufacture had, of course, to be preceded by the accurate working out of practical analytical methods. One of the best proofs of the general demand for such methods, chiefly for use in metallurgy and mineral chemistry, is that even in the year 1686 a technical laboratory was erected by Charles XI. of Sweden. Its objects were to determine the value of various natural products, and also to conduct experiments upon the production of chemical preparations.

The scientific investigations upon the chemical nature of acids and bases, and the increased use of them which resulted, caused attempts to be made to

produce them profitably on a large scale. In this way was laid the foundation of the acid manufacture, now such an important industry. According to Boyle's statement, nitric acid was prepared from saltpetre in special distilleries. The production of fuming sulphuric acid from sulphate of iron was chiefly carried out at Nordhausen in the Harz, while the preparation of sulphuric acid by burning sulphur with addition of nitric acid was first practised about the middle of the eighteenth century in England. The glass globes used in this process were soon replaced by leaden chambers ; these were first employed in Birmingham, and until recently were indispensable for all sulphuric acid factories. With the continually increasing use of soda for the manufacture of soap, glass, etc., the question arose, in what manner this important substance could be prepared from easily accessible sodium compounds, in particular from common salt. It was mainly Duhamel de Monceau who strove in various ways to effect a solution of this problem. Although his experiments were not crowned with success, they yielded important material, with which later chemists, Leblanc among others, were able to carry out the work successfully.

Various improvements, not perhaps very considerable ones, were introduced into metallurgy. There may be specially mentioned the extraction of zinc from calamine (due to Marggraf), and the working of individual metals, such as the engraving, tinning, and gilding of iron and the silvering of

copper, processes in the improvement of which Boyle and Kunkel took the chief share.

In dyeing the endeavour may be noticed, on the one hand, to obtain new dyes, and, on the other hand, to study the process of dyeing itself. The result in the former direction was the preparation of Prussian blue as a dye, and of mosaic gold and Scheele's green as pigments; the researches in the other direction resulted in the division of dyes into two classes, according to whether they might be fixed on the fabrics with or without mordants.

It has already been mentioned (p. 15) that the preparation of porcelain was known very early among the Chinese, but that among other peoples there are no indications of a similar knowledge. The accidental discovery of porcelain falls in this period, and it was soon manufactured on a large scale, but in strict secrecy, at Meissen. The investigation of Réamur and Macquer eventually solved the problem of the production of porcelain, and this resulted in the establishment of the manufacture in France, especially at Sèvres.

Organic Compounds.

The knowledge of organic preparations increased considerably in this period, although no advance is to be noticed in the views upon their real composition. Nevertheless, the mass of material became so large that it was possible for Lavoisier to

do a pioneer's work in this division of chemistry. In particular, practical modes of preparation were worked out for alcohol and the various ethers, and some of these compounds were subjected to closer investigation. It did not escape Hoffmann and Macquer, for instance, that the formation of ether from alcohol was connected with the formation of water. The extensive investigations of Scheele added to acetic acid, which had long been known, a series of other acids, some of which occur in Nature, and were isolated by him from vegetable extracts by means of their calcium or lead salts; instances are citric, tartaric, malic, and oxalic acids. He also succeeded, by the application of chemical reactions, in making new compounds of this type; for instance, he prepared oxalic acid by treating sugar with nitric acid, and mucic acid by similarly treating lactic acid. Scheele also succeeded in isolating uric acid from urinary calculi. Characteristic of the extent of the investigations of this chemist and of the acute observation upon which they were based is especially his discovery of hydrocyanic acid (prussic acid) by treating yellow prussiate of potash with sulphuric acid, and it is particularly worthy of mention that he also gave its qualitative composition pretty correctly. In the province of the chemistry of the fats and oils it was also Scheele who isolated glycerine by decomposing olive-oil with litharge. In spite of all this, the current views on the composition of the fats became no clearer, and the full comprehension of

the importance of the discovery of glycerine in regard to the constitution of the fats and oils was reserved for a later time.

Pharmaceutical Chemistry.

The great influences which the iatrochemical period exercised upon the development of pharmacy, as well as the circumstance that a great number of distinguished workers in this period rose from the position of apothecaries, were not without effect upon the development of pharmaceutical chemical knowledge. From various quarters the scientific treatment of pharmacy was assisted by the publication of sound pharmaceutical text-books, like those of Baumé (1762) and of Hagen (1787), and by the foundation of pharmaceutical laboratories.

The number of drugs experienced a considerable increase in this period. Ammonium carbonate, under the name of *englische Tropfen* (English drops), magnesium sulphate (*sal anglicum*), magnesium oxide (*magnesia alba*), and potassium sulphate (*sal polychrestum*) were all used extensively in medicine. Ferric chloride in alcoholic solution enjoyed under the name of 'golden drops' or 'nerve tincture' a great vogue; kermes, Hoffmann's drops, and basic lead acetate, diluted with water, found medicinal use under the name of Goulard's water. The antiseptic properties of many chemical preparations, such as the mineral acids, ferrous sulphate, alum, etc., were brought into prominence by various chemists, and they were used as antiseptics in some cases.

PART II

CHAPTER I

THE PERIOD OF LAVOISIER

As a result of the pioneering work of the French chemist Lavoisier during the time from 1775 to 1780, the most important object of chemical investigation came to be the examination of the relations by weight of the reacting substances to the reaction products in chemical reactions. So far these relations had generally been neglected, and only one or two investigations are known in which the relations by weight were determined. As an instance may be mentioned Black's work on the calcination of *magnesia alba* (p. 86).

One of the most important results of Lavoisier's quantitative researches was the definite proof of the elementary nature of various substances which had been previously regarded as compound ; among these were the metals, sulphur, and phosphorus. On the other hand, it was also possible to recognize as compounds substances like sulphuric acid, phosphoric acid, and the metallic oxides, which the sup-

porters of the phlogistic theory had considered elementary. We see, therefore, that the work of Lavoisier effected a complete reversal of the chemical views prevailing at the time. That such a reversal occurred comparatively rapidly is chiefly due to the exact investigations of Lavoisier and his pupils, and also to the fact that the balance is a reliable auxiliary which puts into every one's hands a means of control to which no exception can be taken.

The duration of this period we shall consider to be till the year 1828, when the synthesis of urea drew the attention of chemists to a new field of research, which was successfully worked out in the course of the nineteenth century.

Biographical.

Antoin Laurent Lavoisier was born in 1743, and was therefore a contemporary of Scheele. The excellent education which he received gave him a splendid opportunity to perfect himself in mathematics and physics ; he received his instruction in chemistry from Rouelle, who stood in specially high repute as a teacher.

Lavoisier's first chemical work was performed in 1770, and was even then of a quantitative character. He attempted to prove by the balance that the earth formed when water is boiled does not arise from the water, but from the glass of the vessel. The favourable results which the balance yielded to him in this research may very possibly have deter-

mined his later investigations upon the processes occurring during the burning of substances and during the calcining of the metals. The exact treatment of this problem with the aid of the observations of Priestley and Scheele on oxygen led him in 1777 to propose a new theory of combustion. He was elected a member of the French Academy at an early age, and his career soon became a brilliant one. He did not, however, escape the envy of his fellow-citizens, and was executed, upon trumped-up charges, at Paris, on May 8, 1794, a victim of the French Revolution. His work is published for the most part in the *Mémoires de l'Académie Française.*

Of his contemporaries three especially deserve mention — **Guyton de Morveau,** Berthollet, and Fourcroy. The first of these, born at Dijon in 1737, occupied himself at first with the study of law, but soon turned to chemistry. To Morveau is due the first attempt to introduce a rational nomenclature of chemical compounds in place of the designations, vague and leading to all kinds of misunderstanding, then in use (*cf.* p. 106). His successful activity on the founding of the École Polytechnique, at which he became Professor, also deserves especial mention. He was one of the most influential members of the National Assembly, but unfortunately made no effort to check the excesses of the Revolution. He died in Paris in 1816.

Claude Louis Berthollet was born in 1748 at Talloire, in Savoy. In 1772 he took up his abode

in Paris, and was elected to the Academy in 1780. From then he showed great activity in the most various branches of chemistry. At first he was a follower of Stahl's theory of phlogiston, but after 1785 became a convinced supporter of the theory of combustion of Lavoisier. Berthollet became a teacher at the École Polytechnique in Paris in 1794. He possessed a striking talent for organization, which found employment in various inquiries initiated by Napoleon or otherwise undertaken for the public good. In his later years he lived at Arceuil, near Paris, where he died in 1822. Various experimental investigations are due to him, dealing with ammonia, prussic acid, sulphuretted hydrogen, and potassium chlorate, and his theoretical speculations on chemical affinity also deserve mention, as they were then much in vogue, and their after-effects extend even to our own time.

Antoine François Fourcroy was born in the year 1755. He belonged to a poor family, and so was obliged at first to earn the means for his studies. His work, however, soon attracted general attention to him, so that in 1784 he became Professor at the Jardin des Plantes in Paris, in succession to Macquer. He was elected a member of the French Academy in the following year. During the French Revolution he also became prominent as a politician, acted upon the committee of public instruction during the Reign of Terror, and later, under Napoleon, took over the department of public instruction. Chemistry

owes its rapid rise in the following years in no small degree to his influence. In common with Lavoisier, Berthollet, and Guyton de Morveau, he founded in 1789 the *Annales de Chimie.* He died in 1800.

With these three contemporaries of Lavoisier may also be grouped some other important French chemists. **Vauquelin,** born in 1763 at Hébertot, in Normandy, was at first an apothecary, and as such entered Fourcroy's laboratory, where he soon became Fourcroy's collaborator. After the latter's death he obtained his post as Professor at the Jardin des Plantes. His death occurred in 1829. Vauquelin's researches were of the most varied character, as well as his work in the province of organic chemistry, which led to the discovery of quinic acid, asparagin, camphoric acid, etc. ; he was also active with equal success in inorganic chemistry, and discovered chromium and beryllium oxide.

Joseph Ludwig Proust, born in 1755 at Angers, was at first an apothecary, being chief of the dispensary at the Salpêtrière Hospital in Paris ; later on we find him as a teacher in various Spanish Universities. At this time he vigorously opposed Berthollet's view that substances unite in compounds in continuously varying proportions, which change according to the conditions of reaction. As Spain also did not withstand Napoleon's thirst for conquest, he found himself during the war in 1808 deprived of his well-equipped laboratory and of his post. This reduced him to a precarious state

of want, from which he was only removed by his election to the French Academy. His investigations led to much the same result as those of Richter; he often emphasizes the law of combining proportions, without, however, endeavouring to become clear as to its cause.

Joseph Louis Gay-Lussac was born in 1778 at St. Leonard. His introduction into chemical science was effected by Berthollet, and his physical and chemical knowledge soon drew upon him the attention of his contemporaries. In carrying out his inquiries he shrank from no danger, as is shown by the fact that for the purpose of physical observations he sometimes made very hazardous voyages by balloon. In the year 1808 he became Professor of Physics at the Sorbonne, in 1809 also Professor of Chemistry at the École Polytechnique, and in 1832 Professor of General Chemistry at the Jardin des Plantes. From his varied investigations all branches of chemistry received considerable benefit. His name is closely connected with the law of gaseous volumes, with the law of variation of gaseous volume with temperature, and with the investigation of iodine, cyanogen, and fulminic acid, as well as with a large number of analytical methods. On this latter point it may be mentioned in particular that Gay-Lussac is to be regarded as the founder of the titration method in analysis. His death occurred in 1850.

P. L. Dulong, born in 1785 at Rouen, occupied himself with purely chemical work, as well as with

his physico-chemical researches upon atomic heats. He discovered, in 1811, the chloride of nitrogen, a discovery for which he had to pay with the loss of an eye and several fingers ; he also worked on the oxygen compounds of phosphorus and nitrogen. He died in 1838 as Director of Studies at the École Polytechnique at Paris.

T. A. Petit, the collaborator with Dulong in the research on the atomic heats of the elements, belonged in respect of his work more to physics than to chemistry. He was born in 1791, and died in 1820 as Professor of Physics at the École Polytechnique at Paris.

This concludes the description of the lives of the most conspicuous French chemists, and we will now turn to the biography of those who were active at this time in Germany.

Martin Heinrich Klaproth, born in 1743 at Wernigerode, was by profession an apothecary, and only forsook this calling in 1787 in order to give his whole attention to chemical studies. This change was occasioned by his election to the Berlin Academy, and when in 1809 the University of Berlin was founded, he was the first to hold the newly-created Chair of Chemistry. His investigations display classical care and thoroughness. They were undertaken chiefly in the department of analytical chemistry. This thoroughness in his work was not the least decisive factor in enabling him to make the discoveries of new elements ; we owe to him those of uranium, titanium, and zirconium.

Jeremias Benjamin Richter was born in 1762 at Hirschfeld, in Silesia. He was at first Mining Secretary at Breslau, and afterwards Mining Assessor and Chemist to the porcelain manufacture in Berlin. His researches lay mostly in the field of stoichiometry, and are remarkable for painstaking thoroughness and exactitude. Unfortunately his literary style is extremely obscure and confused, and is also to some extent further distorted by the use of phlogistic expressions, so that his work was at first completely overlooked. It was first brought into comprehensible form through the efforts of G. E. Fischer, who put together Richter's figures in a plain table of equivalent weights. In this way it happened that the latter did not obtain the recognition they deserved until long after Richter's death, which occurred in 1807.

Eilhard Mitscherlich, born in 1794 in Oldenburg, devoted himself at first to Oriental and linguistic studies, but he also pursued the study of the natural sciences, and came into close relations with Berzelius, whom he followed to Stockholm in 1819. In the year 1821 he became Klaproth's successor at the University of Berlin, and was active there until his death in 1863.

In England at this time the most important chemists were Henry, Kirwan, Hatchett, and Dalton. Although the labours of the first three greatly advanced particular branches of chemistry, yet in the review of general chemical progress they

are not of decisive significance, so that here their names may be just mentioned. Dalton's work, on the contrary, has had so great an influence upon chemical views that we must consider his career a little more closely.

John Dalton was born in the year 1760 at Eaglesfield, in Cumberland. He was the son of a poor weaver, and so was obliged even in his youthful years to earn his bread by private teaching. At first a mathematician and physicist, he soon turned to chemistry, which he led into new paths by his important work on the atomic theory. In 1793 he became lecturer on mathematics and physics at a college in Manchester. His discovery of colour-blindness was also made about this time. After 1799 he still remained only a private tutor, leading (probably from his hard up-bringing) a very modest life. He died at Geneva in 1829.

In Sweden we find sound representatives of chemical science in Eckeberg and Grau, but in the brief space of this account they can only find mention. We must consider more fully, however, the life of **Johann Jakob Berzelius,** one of the greatest chemists that ever lived. He was born on August 29, 1779, at Westerlösa, in Sweden, being the son of a schoolmaster in that place. Even in his early years he showed a very marked liking for chemistry, but his first teachers could not give him what he expected of this science, and he turned, dissatisfied, to the study of medicine. His interest

in chemistry remained so great, however, that he did not completely neglect it ; on the contrary, his scientific work was principally concerned with chemical ideas, and his nomination as Associate Professor of Medicine, Botany, and Pharmacy was due to his researches upon the action of the galvanic current upon salts. He became, later, Professor of Chemistry and Pharmacy in the University of Stockholm, exchanging this position for the Chair of Chemistry in 1815. In the year 1808 he was elected a member of the Academy of Science of Stockholm, and became its permanent secretary in 1818. In the same year he was made a knight by Charles XIV., and in 1835 raised to the peerage. His strenuous life was closed by death on August 7, 1848. The brilliant researches which he carried out, and his useful activity as a teacher, obtained for him a number of pupils, of whom Rose, Mitscherlich, Wöhler, and Christian Gmelin may here be mentioned as the most famous. It can be understood that by this following of distinguished scholars the ideas, thoughts, and theories of Berzelius were carried into all countries, and that these therefore exercised a striking influence upon the further development of chemical investigation.

The Theory of Combustion of Lavoisier.

The researches of Lavoisier upon the quantitative relations in chemical reactions, which were mentioned in the introduction to this chapter, led this

investigator to set up his theory of combustion or theory of oxidation. Since this overthrew the Stahl phlogistic theory prevailing at that time, and since the whole following period up to the present day is dominated by the ideas of Lavoisier, it will be most fitting to begin the detailed description of the advance of chemistry during this period with an account of this theory.

Lavoisier himself in 1777 summarized his theory of combustion in the following three statements :

1. Substances only burn in pure air.

2. The latter is consumed in the combustion, and the increase in weight of the substance burnt is equal to the decrease in weight of the air.

3. The combustible substance is by its combination with pure air usually turned into an acid, the metals, on the contrary, into metallic calces.

That in atmospheric air there is something which combines with a substance during its combustion was not, however, first stated by Lavoisier. We find, on the contrary, various indications of such an opinion. Mayow's view (p. 75), for instance, comes very near the truth, since he thought that the *spiritus nitro-aërus* present in the air essentially conditions combustion, and that in calcination this substance combines with the metal. The uncontested merit of Lavoisier, however, is that, in opposition to all earlier statements, he not only expressed an idea which could explain certain phenomena, but that he also verified it in its generality by a series of brilliant and exact investigations. By this

he proved at the same time that he was not standing upon purely speculative foundations, but that he controlled his theories by experiments which prompted fresh ideas in their turn. In this way it was possible that, revolutionary as the above-quoted sentences were for the prevailing phlogistic views, they could yet successfully oppose all the objections which at first were raised against them. Lavoisier's theory just furnished the means of explaining a whole series of chemical processes in a simple manner, and so it obtained for itself in such a comparatively short time the recognition of a very wide circle of chemists.

The Classification of Elements and Compounds.

In the course of time, as a result of numerous investigations of various kinds, such an increase in the number of chemical compounds took place that gradually the need arose to attempt a rational classification of the elements and compounds. Such an arrangement is due to Guyton de Morveau (p. 97), and is founded mainly on Boyle's definition of the elements (p. 63). Morveau distinguished five classes of elements. In the first he placed, besides heat and light—not generally recognized as elements—oxygen, hydrogen, and nitrogen ; in the second, those which are able to form acids—*i.e.*, sulphur, phosphorus, and carbon, as well as the hypothetical radicles of hydrochloric, hydrofluoric, and

boric acids; the metals formed the third class, the earths the fourth, and the alkalis the fifth.

The counterpart to these elements was offered by the compounds, among which he distinguished binary and tertiary combinations. To the former belonged the acids, and these he designated with the common word *acide*, followed by the special name of the acid concerned—*e.g.*, *acide carbonique*, *acide sulphurique*, etc. In the case of those containing less oxygen the ending *-eux* was used instead of *-ique*—*e.g.*, *acide sulfureux.* He further reckoned among the binary compounds the bases, to which he applied the common term *oxyde*, besides sulphuretted hydrogen, the metallic sulphides, and the compounds of the metals with each other. The chief representatives of the ternary compounds were the salts. He took their generic names from the acids from which they are formed, and their specific names from the bases contained in them—*e.g.*, *nitrate de plomb*, *sulfate de baryte.* As may be seen from this short sketch of Morveau's arrangement, it was so fortunately chosen that it has been possible to adhere to it in a general way up to the present time.

THE LAW OF MULTIPLE PROPORTIONS.

We will now turn to the consideration of the progress which chemical science has to record as a result of the fortunate investigations of Lavoisier, in which the balance was employed in the most extensive way as an auxiliary.

The numerous quantitative investigations which followed those of Lavoisier soon led to the observation that every element could combine with another element only in definite proportions by weight. The actual occasion for this observation was given by Dalton's work on the composition of ethylene and methane, in the course of which he was able to show that the quantities of hydrogen in these two substances are in the ratio 1 : 2. This research was followed by those on the quantitative composition of carbon monoxide and carbon dioxide, and of nitrous oxide, nitric oxide, nitrous acid, and nitric acid. In all these compounds a regularity of composition was found, and Dalton was able to found upon it the **Law of Multiple Proportions,** which states that *when different quantities of an element chemically unite with one and the same quantity of another, these quantities always stand to one another in a simple ratio which is expressible in whole numbers.*

THE ATOMIC THEORY.

His endeavours to explain these observations as satisfactorily as possible then led Dalton to develop his atomic theory. Even the Greek philosophers had expressed the idea that substances consist of ultimate particles, the atoms, which cannot be divided further. Dalton applied this hypothesis to the law of multiple proportions by simply substituting absolute for relative numbers. In this

way he would say of carbon monoxide and carbon dioxide, for example, that in the former one atom of carbon is combined with one atom of oxygen, while in the latter one atom of carbon is combined with two atoms of oxygen. These researches were carried out in 1802 and 1803, but they were not fully published till 1808, when they appeared in the first volume of the *New System of Chemical Philosophy*.

The central point of the whole of Dalton's atomic theory may be expressed in the following two sentences :

1. Every element consists of atoms similar in kind and of unvarying weight.

2. Chemical compounds are formed by union of the atoms of different elements in the simplest numerical ratios.

It must be concluded, however, from numerous indications that the historical development of Dalton's work did not occur in the manner here described, but that, on the contrary, Dalton arrived at the atomic theory by a purely deductive path, and only carried out the experimental investigations as a confirmation of the opinions so formed.

✓ An immediate consequence of the atomic theory was the attempt to determine as accurately as possible the proportions by weight in which the elements unite to form compounds, and so to derive the relative atomic weights. Dalton himself attacked this problem, but was obliged for the purpose to make certain postulates, which he sum-

marized in the following statements; in them compounds of two elements are considered:

'When only one compound of two elements, A and B, is known, it is to be supposed that it consists of one atom of the one element and one atom of the other: $A + B$, a binary compound or atom of the second order (Dalton regarded an elementary atom as an atom of the first order).

'When two compounds are known which are composed of two elements, A and C, their composition can be expressed by the symbols $A + C$ and $A + 2C$ (ternary compound or atom of the third order).

'If the composition of three compounds of two elements, A and D, has to be decided, probability is in favour of the following compounds: $A + D$, $A + 2D$, $2A + D$.'

Besides these there were, according to Dalton, also atoms of the fifth order (*e.g.*, $A + 3E$), etc., though the simplest proportions were the most favoured. Compounds in which the numbers of atoms were in ratios such as 2 : 3 or 2 : 5 he explained to have arisen from two atoms of the higher orders, as, for instance, nitrous acid from an atom of nitric oxide and an atom of nitric acid.

These considerations led to the obvious conclusion that the atomic weight of a compound is equal to the sum of the weights of the elementary atoms composing it. In determining the relative atomic weights of the elements Dalton took the following course. He determined, for instance, the

ratio of the quantities of hydrogen and oxygen in water, and then set the weight of the hydrogen as unity, referring the oxygen value to it. In a similar way he determined the value for nitrogen from the composition of ammonia, and that of carbon from the analysis of carbon monoxide and carbon dioxide, in the latter case using the oxygen value obtained from the composition of water. By this means he found the following numbers :

Hydrogen	1·0
Oxygen	6·5
Nitrogen	5·0
Carbon	5·4

Although there is considerable inaccuracy in these figures, the principle for atomic weight determination was correct. The development of Dalton's atomic hypothesis was in general so illumining and clear that it found a favourable reception almost everywhere among the chemists of the time.

Gay-Lussac's Law of Volumes and Avogadro's Hypothesis.

A few months after Dalton had explained his atomic theory in the *New System of Chemical Philosophy*, Gay-Lussac published investigations which were concerned with the volume relations of gases. This chemist found that from 2 volumes of carbon monoxide and 1 volume of oxygen are formed 2 volumes of carbon dioxide, and 2 volumes of ammonia from 1 volume of nitrogen and

3 volumes of hydrogen. These observations agree also with various experimental results obtained by earlier investigators, and led Gay-Lussac to set up the **law of volumes,** which he formulated in the following way: '*Two gases always combine in simple proportions by volume, and the contraction which they experience, and therefore also the volume of the product formed when it is gaseous, stands in a simple relation to the volumes of the constituents.*'

Gay-Lussac also specially points out at the end of his paper that by the supposition of a similar molecular condition in all gases their similar behaviour towards pressure and temperature is explained, and that his observations not only are in agreement with Dalton's atomic hypothesis, but also offer considerable support to it. This opinion did not, however, obtain agreement from Dalton. The reason for this was that if an atom of nitric oxide consists of an atom of nitrogen and an atom of oxygen, and if in equal volumes equal numbers of atoms be supposed, then by the union of 1 volume of nitrogen with 1 volume of oxygen 1 volume of nitric oxide must be formed, not 2, as Gay-Lussac and Henry had found.[1] According to this, a similar molecular condition of all gases would be impossible, and it is not difficult to see that in this point lay a real difficulty.

[1] The totally unjustified reproach which Dalton made that Gay-Lussac had worked badly very probably led to the idea that Dalton enviously desired to detract from Gay-Lussac's services to the science. At the same time, the account given above shows that Dalton's objections had a foundation in fact.

The Italian physicist **Amadeo Avogadro** showed a way in which it was possible to explain these contradictions. He distinguished between *molécules intégrantes* and *molécules élémentaires*, and on account of the similar behaviour of gases towards pressure and temperature he supposed that in equal volumes of all gases are contained equal numbers of molecules.

According to this hypothesis, when a substance, elementary or compound, becomes gaseous, the gas consists not of indivisible particles, but of the *molécules intégrantes*, which are composed of the *molécules élémentaires*. If, therefore, a mixture of equal volumes of oxygen and nitrogen unite to form the same volume of nitric oxide, and if the total volume contains the same number of molecules, then the combination cannot have occurred from union of molecules previously separate. This experimental fact can only be explained by supposing that the molecules both of nitrogen and oxygen are each composed of two *molécules élémentaires*, which break apart from one another and reunite in unlike pairs, so that the same number of molecules is present before and after the combination. The difference in the composition of the gaseous mixture is simply that at first it consists of dissimilar, afterwards of similar, molecules.

In 1814 there appeared in the *Annales de Chimie et de Physique* (xc., 43) a paper by Ampère upon the same subject. In it the author endeavoured at the same time to explain the crystalline form of

substances by the position of the *molécules élémentaires* in the *molécule intégrante*. On the whole, the writings of these two scientists received at first but little attention from their contemporaries.

In the years 1791-1802 J. B. Richter made the observation that on mixing two neutral salts the neutrality remained, even when double decomposition took place. He concluded from this that the quantities a and b of two bases which were neutralized by a certain quantity of an acid were also neutralized by the same quantity of another acid, and *vice versa* the weights of two acids which are saturated by a certain quantity of a base require for neutralization the same amount of another base. Richter further examined the precipitation of metals, and determined the quantities of the metals which precipitate one another from their solutions; the numbers so obtained he employed to determine the oxygen content of the oxides. It should also be mentioned that Richter first used the term 'stoichiometry,' meaning thereby the determination of the proportions in which substances combine. As has been stated above, Richter's publications are written in a very incomprehensible style, so that they first came to general knowledge through the efforts of Fischer, who brought them into a form more easy to understand. Fischer, in 1803, united Richter's tables in a single table which he employed in the following way: 'It is necessary to determine only the relative quantities of one acid towards the various bases, then it is sufficient to

become acquainted with the relative quantity of one single compound of every other acid with a base, and by an easy calculation the proportional quantities of the acids in all other compounds can be obtained.' This was, however, no other thing than a table of equivalents.

Atom and Equivalent.

In 1814 Wollaston sought to show—chiefly, at any rate, by reason of Richter's investigations—that the determination of the number of atoms in a compound was uncertain and arbitrary, and proposed to replace the idea of atoms by that of equivalents. The name 'equivalent' was used by him for the first time. To begin with, he made the mistake of using the term 'equivalent' quite in the sense of 'atom'; this led to the erroneous supposition that the atoms were equivalent. We shall see later what great confusion this paper of Wollaston's caused in chemical circles, and that it needed vigorous conflicts to effect the strict separation of the ideas involved in the terms 'atom' and 'equivalent.'

Electro-chemical Theories.

Towards the end of the eighteenth century came Galvani's famous discovery in the year 1779 of electric action upon the muscles of frogs, and the further development of this by Volta led to voltaic cells and galvanic batteries. As in this way a source of electricity was discovered, it was not long

before the effect of the electric current upon various chemical substances was studied. Nicholson and Carlisle observed in 1800 that if the galvanic cell is discharged through water the latter is decomposed into its constituents, oxygen and hydrogen. It has already been mentioned (p. 75) that Ritter tried to maintain the elementary nature of water by explaining hydrogen to be water with positive, oxygen water with negative, electricity. The electrolysis of water was followed by that of aqueous solutions of alkalis, which was principally effected by Davy and by Berzelius. We shall become more fully acquainted with the practical results of these investigations later, in treating of the metals. They will only receive mention here in so far as they were responsible for the development of theoretical views.

As to the origin of the electric current, Volta advanced the opinion that the mere contact of two heterogeneous bodies sufficed to place them in opposite electrical states. Davy also held the same view, and based upon it his theory of the dependence of chemical affinity upon electrical state (*Phil. Trans.*, 1807, p. 39). The most active opponent of this contact theory of Volta and Davy was Ritter, who in his *Electrischen System* sought to show that simultaneously with the origin of an electric current chemical decompositions take place, and that therefore the electrical phenomena are a result of chemical processes. Berzelius imagined electricity to be a general property of matter, and supposed each atom to have two opposite poles. The atoms do not

contain equal quantities of electricity, but the electricity of one pole predominates over that of the other, so that the atom (and therefore also the element) is either electro-positive or electro-negative. When two elements unite, their opposite poles neutralize each other; but if an electric current is allowed to act on a compound, the single atoms obtain an electric charge again, and the compound is decomposed into its constituents.

Upon these ideas Berzelius built his so-called dualistic theory. He says in his *Lehrbuch der Chemie*, vol. iii., p. 77: 'Every compound substance, whatever the number of its constituents, can be separated into two parts, of which one is electro-positive, the other electro-negative; so, for instance, sodium sulphate is not composed of sodium, sulphur, and oxygen, but it consists of sulphuric acid and soda, which, again, can each be separated into a positive and a negative constituent.'

Such were the views of Berzelius as to the constitution of compounds in general. His opinion on the structure of bases, acids, and salts he expressed as follows: 'In the oxides the metals form the electro-negative constituent, in the acids the metalloids, and in the salts the anhydrous bases are the electro-positive, and the anhydrous acids the electro-negative, constituents.' By a slight extension it was then possible for him to explain the double salts in this dualistic manner, regarding one salt as the electro-positive and the other as the electro-negative constituent; for instance, in alum he

termed the potassium sulphate the positive and the aluminium sulphate the negative constituent. It must not be overlooked, however, and it shall be especially emphasized here, that the foundation of this dualistic theory took place at an epoch when all the acids were still regarded as compounds containing oxygen. We shall find later that on account of the dualistic theory it cost many a hard-fought battle to persuade Berzelius and his supporters of the existence of acids which did not contain oxygen. The outlines of this electro-chemical theory were set out by Berzelius in 1812; its complete elaboration occurred in 1819.

Chemical Symbols.

The need of a simple system of chemical symbols became continually more evident to Berzelius during the working out of the preceding views. He was not the first to have an idea of this kind, for several years previously Dalton had proposed the introduction of particular symbols for the different elements. He indicated oxygen, for instance, by ○, hydrogen by ⊙, nitrogen by ⦶, sulphur by ⊕. By correctly placing together these symbols it was possible to picture the compound concerned. For the anhydride of sulphuric acid, for instance, this gives the following symbol: . It is obvious that this system was too complicated and too unwieldy ever to come into general use. To get

over the difficulty Berzelius developed a system of chemical symbols in which a letter stood for every element, preferably the initial letter of the Latin name of the element concerned—*e.g.*, for nitrogen (*nitrogenium*) N, for sulphur (*sulfur*) S, for hydrogen (*hydrogenium*) H. In the case of those elements which have names beginning with the same letters some further letter was added from the rest of the word—*e.g.*, mercury (*hydrargyrum*) Hg, antimony (*stibium*) Sb. To indicate compounds these symbols were simply placed side by side, the number of atoms of each element in the compound, if more than one, being shown by suffixing a number, thus : sulphurous acid SO_2, carbonic acid CO_2.[1] With the help of this system of symbols it was also possible to express the dualistic constitution of individual compounds—for instance, sodium carbonate $Na_2O.CO_2$—and this was of course of great importance from the point of view of Berzelius.

Berzelius did not at first use this mode of writing quite as above described, but indicated those elements which occur as double atoms in compounds by drawing a line through the symbol for a single atom—*e.g.*, water ~~H~~O. This was probably the cause of the resistance which at first was opposed to the introduction of the system of symbols of Berzelius, for when he discarded a mode of writing so calculated to lead to confusion, and introduced the universal designation by numbers described

[1] At first Berzelius also indicated oxygen atoms with dots, sulphur atoms with dashes—*e.g.*, $\dot{C}a$ (for CaO), $\overset{''}{F}e$ (for FeS_2).

above, the system came into general use, and still forms the foundation of chemical formulation.

The nomenclature of Berzelius followed that employed by Lavoisier, Guyton de Morveau, and Berthollet. He divided the elements into metalloids and metals, the oxygen compounds into suboxides, oxides, and peroxides, while he gave the acids different designations according to their degree of oxidation. For the chlorine compounds corresponding to the oxides he used the similar terms, 'subchloride,' 'chloride,' and 'perchloride.'

The Electrolysis of the Alkalis.

As has already been mentioned (p. 118), in the development of the dualistic views of Berzelius all acids were regarded as oxygen compounds, and, in fact, the whole theory was bound up with the supposition that oxygen is a constant constituent of all acids. Already in the first twenty years of the nineteenth century, however, this opinion was strongly shaken by Davy's researches on the electrolysis of salts of the alkalis. Davy endeavoured to subject an aqueous solution of potash or soda to electrolysis, and the failure of these experiments led him to alter the experimental arrangements so as to allow a strong electric current to act on fused potash. He observed the formation of small drops of a metal which burnt vigorously when brought into contact with air. By maintaining certain experimental conditions he succeeded also in isolating

small quantities of this substance. He noticed that the separation of metallic drops occurs only at the negative pole, while at the same time an evolution of oxygen takes place at the positive pole. As to the properties of the substances formed, it did not escape him that they could reduce metallic oxides, and that they regenerate the alkali when they burn in oxygen. For this reason he regarded potash and soda as metallic oxides, and the new substances he had discovered as metals, a view favoured by their well-marked metallic lustre. He proposed for them the names 'potassium' and 'sodium.' It should also be mentioned here that in 1808 Gay-Lussac and Thénard succeeded in obtaining these metals in a purely chemical way by reducing the hydrates with metallic iron, and so furnished an exact confirmation of Davy's researches upon these substances.

Chlorine and Iodine.

As in this way the views on the nature of the alkalis were made more clear, so also were those on chlorine. Hydrochloric acid, like all other acids, was considered to contain oxygen, and so the chlorine obtained from it by oxidation was oxidized hydrochloric acid. This supposition gave rise to thorough-going investigations on the reduction of chlorine. All these experiments, which were carried out by Davy and by Gay-Lussac and Thénard, were however, fruitless; chlorine could not be reduced even when charcoal was heated to whiteness in the

gas. When in 1808 Davy also found that sodium on combustion in chlorine gas gives common salt, he began openly to maintain the opinion that oxidized hydrochloric acid—*i.e.*, chlorine—is a simple substance, and that the oxygen obtained when chlorine is led over a heated metallic oxide does not come from the gas, but from the oxide; he named this element chlorine. But according to this, hydrochloric acid is an acid in which hydrogen is the base and oxidized hydrochloric acid takes the place of oxygen. Berzelius opposed this view vigorously, and made great endeavours to overcome it. He was far too much possessed by the idea of the value of the general applicability of his theory to make concessions at the expense of its unity. We find in his replies to Davy less of the experimenter than of the defender of a system; in fact, most of the objections are supported by arguments from analogy.

Davy's views upon the elementary nature of chlorine were greatly strengthened by the important researches of Gay-Lussac upon iodine in 1813. Berzelius himself was persuaded of their correctness when he carried out his investigations upon the cyanides containing iron. He plainly expresses himself to this effect in 1820 in connexion with hydrothiocyanic acid: 'From what I have said concerning this hydrogen acid and also concerning hydrocyanic acid, it will be readily seen that all the phenomena connected with them can only be explained upon the theory which has recently been

put forward for hydrochloric acid.' In the same year he recognized that ammonia does not contain oxygen, and in 1825 he designated fluorine as a salt-forming element like chlorine and iodine. For these elements he introduced the term 'halogens'; their salts he sharply distinguished from those that contain oxygen, using the terms 'haloid salts' and 'amphoid salts' to indicate the two classes.

The Atomic Weights of Berzelius.

We left the stoichiometrical work of the chemists of this time with the equivalents of Wollaston to occupy ourselves with the influence of electricity upon the development of chemical theory, which led to the electro-chemical theory of Berzelius. Now that we have considered this question we will return to the investigations upon multiple proportions.

Berzelius endeavoured to blend Gay-Lussac's Law of Volumes with the atomic theory by supposing that when any elementary substance assumes the gaseous state a certain volume corresponds to each atom; he termed these smallest fractions 'atomic volumes.' In this way he was enabled to determine the relative atomic weight of hydrogen and oxygen from the fact that water consists of 2 volumes of hydrogen and 1 volume of oxygen. The law of volumes therefore served Berzelius as a means of deriving the atomic weights of numerous elements from the atomic composition of different substances. It may be added, as a proof of the

enormous capacity for work of Berzelius, that besides his activity as a teacher and his other theoretical and literary work he determined in a little more than ten years the atomic weights of about fifty elements from almost two thousand different compounds, the analyses being carried out with his own hands. The following values, dating from the year 1818, may serve as examples of the exactness of his work. He referred them to oxygen (the 'pole of chemistry') as 100; they are here recalculated for oxygen = 16, and the present values are added in brackets:

Carbon	12·2 (now 12·0).
Oxygen	16·0 (now 15·96).
Iron	109·1 (now 56·0 = $\frac{1}{2}$ of 112).
Sodium	93·5 (now 23·0 = $\frac{1}{4}$ of 92).

The work of Berzelius received a considerable extension and confirmation when in 1819 two important discoveries of a physico-chemical nature were made. One of these concerns the relations between the atomic weights of the elements and their specific heats, while the other draws attention to the connexion between crystalline form and chemical constitution.

Dulong and Petit made the discovery that the specific heats of solid elements are almost inversely proportional to their atomic weights; from this they derived the statement that the atoms of elementary substances possess the same capacity for heat. This discovery is naturally a very important aid in determining the relative weights of the atoms,

for it means that the product of specific heat and atomic weight is a constant quantity ; this quantity was termed by Dulong and Petit the atomic heat. In order to find any particular atomic weight it is therefore only necessary to determine the specific heat of the element concerned, and then calculate the atomic weight from the atomic heat. Dulong and Petit carried out this determination in numerous instances, and it then appeared that exceptions occur in the case of some of the non-metals, the explanation of which has only recently been furnished ; on the whole, however, the investigations of these two workers among the metals extended and confirmed the results of Berzelius.

E. Mitscherlich made the important discovery that crystalline form and chemical constitution stand in a certain relation to each other, and so explained the occurrence of isomorphous crystals of different substances to be due to a similarity of chemical constitution. His investigations extended chiefly over the phosphates and arsenates, the selenates and sulphates, the oxides of magnesium and zinc, and those of iron, chromium, and aluminium, together with their salts. From these researches upon isomorphism Berzelius sought to derive the atomic weights of elements from the isomorphism of their compounds by regarding as the relative atomic weights the quantities of the elements (referred to hydrogen or oxygen as unity) which could replace one another without changing the crystalline form.

This extension of the possibility of atomic weight determination caused Berzelius to make many changes as time went on in the values he had originally found. A direct impulse towards the preparation of a new table of atomic weights was given by his researches upon the constitution of chromic acid and of chromium sesquioxide. The proportion of oxygen to chromium is 3 : 1 in the neutral chromates, corresponding to CrO_3 as the formula for chromic acid ; for chromium sesquioxide, on the other hand, he found the composition Cr_2O_3—that is, a proportion of oxygen to metal of 3 : 2. The significance of these considerations lies in the fact that the atomic weights of various other metals will then be only half as great as those hitherto assigned to them by Berzelius ; these halved values also agree with those found by Dulong and Petit. This amended table of atomic weights was published by Berzelius in 1826, and it deserves especial mention that it includes for the first time the atomic weights of nitrogen and chlorine, recognized at last not to contain oxygen.

In spite of all these tables of atomic weights, Berzelius held fast to the assumption that the quantities of the elements occupying equal volumes in the gaseous state are their atomic weights. This opinion was rendered untenable by a method of determining vapour densities published in 1827 by the chemist J. B. Dumas in the *Annales de Chimie et de Physique.* It would lead too far to describe the actual method here, and it may be regarded,

besides, as generally known; we will occupy ourselves, rather, with the influence which it exercised upon chemical science. Dumas determined, according to his method, the specific gravity of the vapours of iodine, mercury, phosphorus, and sulphur, and assumed, like Berzelius, that the ratio between the mutually comparable values obtained in this way would be that of their relative atomic weights. The result was that the values he obtained did not agree with those determined by Berzelius. Dumas found for—

Iodine	123·0
Mercury	101·0
Phosphorus	62·8
Sulphur	96·0

While Berzelius in his table of 1826 gives :

Mercury	202·80
Phosphorus	31·40
Sulphur	32·24

From this comparison it may easily be seen, nevertheless, that simple relations hold between the values found by these two chemists. These results were in themselves calculated to create confusion among the chemists living at that time, and Dumas contributed a great deal to increase this confusion by changing atomic weights in quite an arbitrary manner. It was for this reason that prominent chemists like Gay-Lussac or Liebig towards the end of this period practically denied

the possibility of determining the relative weights of the atoms, and contented themselves with fixing the so-called equivalents.

Chemical Affinity.

In addition to these investigations upon questions raised by the atomic theory, preliminary conclusions were obtained in this period regarding the older question of chemical affinity. The repeated observation that a series of compounds enters into reaction with certain others, while with others it does not, led even in the time of Albertus Magnus (thirteenth century) to the idea that a certain selective affinity must subsist between individual compounds, and to this property the term *affinitas* was applied. Glauber then occupied himself more closely with this question, and endeavoured to make its nature more evident by the figurative expression of love and hate (p. 46). He, as well as Boyle and Stahl after him, arranged series of chemically similar substances of which each was able to displace the next from certain compounds. This mode of expression in the form of series took a shape which persisted for some time in the tables of affinity worked out by Geoffroy the elder, which appeared in 1718. With the increasing development of chemical knowledge these tables of Geoffroy had to undergo continual extension and revision, and the cases continually became more noticeable which could not be included in the series, but occupied an anomalous

position. There was, of course, no bridle set to the imaginations of chemists at that time, and so the most incredible opinions arose. Lemery, for instance, supposed that one of the bodies was provided with sharp points, the other with pores into which the points of the former became fixed, and so a compound was formed. To Boyle, again, is due the idea that the smallest particles of different substances attract one another, and that the degree of this mutual attraction depends upon the form and position of the individual particles. This view led, however, to the erroneous opinion that liquid substances act better than solid, and gaseous better than either. Now and then the attempt was made to bring the force with which these particles mutually attract each other into relation with the general force of gravity. One treatment of the conception of chemical affinity from Boyle's point of view is due to Bergmann (p. 70), but he maintained the erroneous opinion that an acid showed the strongest affinity to that base of which it saturated the greatest amount when forming a neutral salt. Guyton de Morveau brought together all these ideas of chemical affinity in the following six laws :

1. 'Corpora non agunt, nisi fluida.'

2. Affinity is only present between the smallest constituent particles of substances.

3. The affinity tending to cause combination acts only in so far as it predominates over the affinity of cohesion.

4. Two or more substances which by virtue of

combining affinity combine with one another form a whole which possesses new properties completely different from those of either of the substances before combination.

5. The affinities require certain conditions of temperature, which make their action slower or more rapid, destroy it or strengthen it.

6. From the affinity of one substance for another no conclusion can be drawn as to the affinity which will be exerted by a mass composed of both substances with an excess of one of them.

These six laws led Guyton de Morveau to the further rule that chemical affinity is constant, and at the same time independent of the amounts entering into reaction. In contradiction to this, however, Berthollet stoutly maintained that the mass of the reacting substance had considerable influence upon its chemical affinity, and concluded, further, that the chemical effect of a substance was to be considered as the product of its affinity and its mass. This idea had already appeared in 1777 in a book by the Saxon State chemist Karl Friedrich Wenzel, who plainly expressed there the general principle now held in chemical science that the strength of chemical action is proportional to the concentration of the active substance. Wenzel was, therefore, the discoverer of the law of mass action; but, unfortunately, through an oversight of Berzelius, his work did not obtain at that time the recognition it deserved. As regards the share of Berthollet in this very important law, it seems as

though he developed the conception of chemical mass action independently of Wenzel. In working out this idea, however, Berthollet fell into the mistake of not sufficiently regarding the stoichiometric relations of individual substances to one another, and it was owing to this that his ideas met with vigorous opposition at the hands of several chemists (Proust, *vide supra*, p. 99). It required an interval of time of almost half a century in order to bring them into a form of general applicability. This development resulted from the mathematical treatment of the law of mass action by Guldberg and Waage in the year 1867, and in the shape into which they put it it has largely conditioned our present views of chemistry.

Such was the position of chemical theory towards the year 1830. At this time, however, there were made some discoveries which were of such decisive importance for the further development of chemical science that it seems justifiable to consider this the end of one period and the beginning of a new one. These discoveries were the chemical syntheses of some few substances formed in Nature, especially the synthesis of urea by Wöhler (1828). These achievements turned the principal attention of chemists to the department of organic chemistry, and it should be generally known what beautiful results have been obtained in this field especially by the combined labours of theory and practice.

New Elements and Inorganic Compounds.

The speculations previously mentioned gave occasion in many cases to the closer investigation of a number of compounds, and this brought a great increase in experimental material. The fall of the theory of phlogiston first produced a sound division between elements and compounds, and as early as 1789 Lavoisier in his *Traité de Chimie* counts twenty-three elements. It was, indeed, his own work which proved conclusively the elementary nature of well-known metals like iron, zinc, mercury, arsenic, and antimony, and which caused the recognition as elements of a number of so-called metalloids. Among the latter were hydrogen, sulphur, phosphorus, nitrogen, and chlorine. In the case of the two last we have seen that their elementary nature was vigorously contested for a long time, and that very thorough investigations were necessary in order to secure for them general recognition as elements. The number of elements was further increased by the discovery of various new representatives of this class of substances. In 1811 iodine was discovered by Courtois in the ashes of sea-plants, and in 1826 bromine by Balard in the mother-liquors of sea-salt. Both were soon seen to be elements very similar to chlorine. Tellurium was first observed in 1782 by Müller von Reichenstein, and selenium in 1817 by Berzelius. Boron was isolated from boric acid in 1808 simultaneously by Gay-Lussac and Davy, while the discovery of

silicon fell to Berzelius in 1810. In the investigation of the elements carbon, sulphur, and selenium, the phenomenon of allotropy was observed, and it gave occasion to many researches, in which Berzelius especially took a share (p. 149). Potassium and sodium were prepared in 1807 by Davy by electrolysis of their hydroxides, and a short time afterwards by Gay-Lussac and Thénard by reducing these compounds with metallic iron (p. 121). These researches were followed by the isolation of barium, strontium, calcium, and magnesium. In 1817 Arfvedson, a pupil of Berzelius, discovered lithium in several minerals. Wöhler in 1827 isolated aluminium by acting on its chloride with metallic potassium, and in 1828 beryllium in a similar way. Vauquelin in 1797 recognized chromium as a constituent of lead chromate. In 1783 molybdenum was isolated by Hjelm and tungsten by D'Elhujar, after their existence had been predicted by Scheele and by Bergmann. Although platinum was introduced into Europe from South America as early as the middle of the eighteenth century, it was not until 1804 that palladium was isolated by Wollaston from native platinum. The further examination of native platinum then led to the discovery of the other elements resembling platinum—viz., rhodium, indium, and osmium.

Along with this increase in the number of elements a systematic treatment of the compounds derived from them had developed. In the case of the non-metals, the different oxides and the acids

derived from them were prepared and investigated. To this subject belong the researches of Gay-Lussac upon chloric acid, those of Davy and Stadion upon hypochlorous acid, and those of Stadion upon perchloric acid; and these were followed by investigations of the corresponding iodine compounds. The various sulphuric acids were closely studied by Gay-Lussac. Davy, Berthollet, and Thénard took an active share in the investigation of the different compounds of arsenic, antimony, and phosphorus. The salts of silver were employed by Davy for the fixation of light impressions, and to the investigation of the cyanogen compounds of iron both Berzelius and Gay-Lussac devoted special care.

Technical Chemistry.

All these researches furnished technical chemistry with a number of new or improved processes. The introduction of continuous working in the sulphuric acid manufacture resulted from the use of Gay-Lussac and Glover towers, by means of which a rational mode of working was first attained. The commercial preparation of soda from rock-salt was due to Nicholas Leblanc, who started the first soda manufactory in the year 1791. Berthollet's investigations on the bleaching action of chlorine prompted the method for preparing bleaching powder due to Thénard in 1799. Towards the end of this period falls also the discovery of ultramarine, effected in 1828 by Gmelin and Guinet simultaneously, and

this substance was not only technically an extremely important dyestuff, but also gave rise to many scientific investigations.

ORGANIC CHEMISTRY.

The theory of combustion of Lavoisier, and his researches relating to it, brought to organic chemistry far-reaching changes and much clearer views. From his investigations Lavoisier arrived at the conclusion that all organic compounds contain carbon, hydrogen, and oxygen as chief constituents, and in a subordinate way nitrogen, phosphorus, and sulphur. The formation of carbon dioxide and water was employed by Lavoisier as a qualitative test for carbon and hydrogen. As a test for nitrogen Berthollet and Lasaignac utilized its transformation into ammonia or sodium cyanide, while they proved the presence of phosphorus or sulphur from the formation of phosphoric acid or sulphuric acid on oxidation. Lavoisier also indicated the correct way to carry out the quantitative analysis of organic substances, for he endeavoured to determine their oxidation products, using as oxidizers compounds which readily part with oxygen, such as mercuric oxide or red lead. In principle, therefore, his process coincides with the present method of carrying out an analysis of that kind, but his statements on this point became public only when his diaries were examined after his death, and as a result of this the quantitative analysis of organic compounds was

still very imperfect at the beginning of the last century, in spite of many extensive researches by Dalton, Saussure, Thénard, Gay-Lussac, and Berzelius. The chief cause of this was that these chemists generally used potassium chlorate as oxidizing agent, until Gay-Lussac introduced copper oxide, the substance still in general use for this purpose. A convenient and simple mode of executing such an analysis did not, however, become possible till Liebig had constructed his three-bulb apparatus, and that in point of time falls within the next period.

The general extension of chemical knowledge and the accompanying increase in the number of known compounds soon necessitated a division of the various substances into separate groups. The observation that a number of chemical compounds occur in plants and animals, while others are found in the mineral kingdom, led to a distinction between mineral, vegetable, and animal chemistry. A classification of this kind is due to Bergmann, who in 1780 divided chemical compounds into organic and inorganic substances. In connexion with this stands the general principle, put forward at this time, that organic substances could not be prepared artificially from their elements, but that, on the contrary, a certain vital force (*vis vitalis*) was necessary for their formation. Berzelius endeavoured to give this classification a still deeper foundation, and accordingly described inorganic substances as binary compounds, in contradistinction to organic

substances, which he considered to be ternary and quaternary. He further supposed that the latter always consist of more than two elements, though this forced him to include marsh gas and other similar compounds among the inorganic substances.

The beautiful researches of Gay-Lussac on cyanogen, which led to its recognition as a compound radicle and to the observation of its analogy with the halogens, led to the supposition that organic compounds consist of certain atomic complexes. From this point of view Gay-Lussac represented alcohol as consisting of ethylene and water, and Döbereiner went so far in the same direction as to regard oxalic acid as consisting of water, carbon dioxide, and carbon monoxide.

The increasing observation at this time of cases of isomerism—*i.e.*, the phenomenon that organic compounds of similar percentage composition may possess different properties—made it evident that the mere knowledge of the empirical composition of a compound could no longer be considered sufficient, but that the connexion between this and the chemical constitution must be sought for in as thorough a manner as possible. This, however, marks the transition to the next period, in which organic chemistry underwent rapidly and independently further development. This rapid growth it owes in part to the perfection of the methods of organic analysis, but chiefly to a number of fortunate speculations which in the course of time led to the building up of structural chemistry.

With regard to detailed knowledge in organic chemistry, it may be mentioned that a considerable number of hydrocarbons was known, including marsh gas, ethylene, etc., and the number was further increased by the method due to Mitscherlich for the isolation of such compounds from crude benzene. This was followed by the formation of benzene from benzoic acid, and this, again, by the preparation of other hydrocarbons from carboxylic acids—for instance, of methane from acetic acid. The salts of the organic acids were exhaustively investigated by Berzelius, for he sought to discover whether they also followed the law of multiple proportions. This work led him to the examination of the polybasic saturated carboxylic acids, especially succinic acid. In 1834 Mitscherlich prepared nitrobenzene by acting upon benzene with nitric acid, and Dumas and Gerhardt (p. 161) recognized it as a substitution product of benzene. These researches resulted in the addition of the radicle 'nitryl' (NO_2) to the halogens and cyanogen.

The technical employment of the knowledge gained in the study of organic compounds rendered important advances possible in the manufacture of various organic products. The manufactures of starch and sugar may be especially mentioned. Although the practical development of the process for converting starch into sugar by treatment with acids is a matter of recent discovery, yet the first observation that sugar is formed from starch under certain conditions was made in 1811 (Kirchhoff).

As early as the end of the preceding century the manufacture of sugar from the sugar-beet was undertaken, probably because of the Continental blockade, which at that time influenced all branches of industry. Until the beginning of the nineteenth century, however, the manufacture was in a more or less precarious condition, although various improvements were introduced into the practical processes themselves. Among these may be mentioned the filtration through bone-ash of the refined syrup, recommended by Figuier in 1811 and by Derosne in 1812, and the vacuum pans introduced by Howard in 1813.

CHAPTER II

THE PERIOD OF THE DEVELOPMENT OF ORGANIC CHEMISTRY

During the period described in the preceding chapter the practice of drawing a distinction between inorganic or mineral chemistry and organic chemistry had become more and more established. This separation was due to the assumption that for the formation of an organic substance a certain vital force was necessary. This opinion was overthrown in 1828 by Friedrich Wöhler, who succeeded in preparing artificially, by heating potassium cyanate with ammonium chloride, the substance urea, which is present in urine, and is, therefore, formed in the human organism. When once a beginning had been made with the artificial preparation of natural products, further syntheses of this kind followed one after another, and this resulted in an unexpected development of this side of chemistry. Lavoisier's view was confirmed—that these substances are all composed of a limited number of elements, and always contain carbon. This was expressed in general terminology by the

use of the expression 'chemistry of the carbon compounds,' as opposed to 'inorganic' chemistry. Strictly speaking, it is, of course, incorrect to make a distinction between organic and inorganic chemistry, for the carbon compounds are compounds of carbon in just the same way as the potassium salts are compounds of potassium, and it is necessary, besides, to assign carbonic acid and its salts to inorganic chemistry. If, however, a division be introduced, then the term 'chemistry of the carbon compounds' is still the most suitable, and the introduction of a special division for these compounds is necessary, if only from reasons of convenience, owing to the enormous number of known chemical substances.

Biographical.

The duration of this period we shall regard as extending to the year 1886, when the promulgation of the dissociation theory of Arrhenius again effected a considerable change in chemical views. Before we concern ourselves with the development of chemical thought in this period, we will endeavour to obtain an idea of the lives of its more important chemists, though by reason of limited space it is only possible to treat of a small number of them.

Justus von Liebig was born at Darmstadt on May 12, 1803. He took up at first the calling of an apothecary, but soon bade farewell to it, and devoted

himself to the study of chemistry, in which he made himself known by his researches on fulminating silver. The fascinating personality of Schelling held him at Erlangen for two years in the spell of the natural philosophy current at that time. Thanks to his strongly marked independence, he freed himself from this influence, and left Erlangen to wend his steps towards Paris, then the centre of chemical science, and so we find him there in 1821 as the pupil of Gay-Lussac, with whom he carried out the important research upon the fulminates. In 1824 he was called, as Professor of Chemistry, to Giessen, where he was active for twenty-eight years, striving hard at the same time for the institution of a rational system of chemical instruction. In 1852 he accepted a call to the University of Munich. His fruitful life was ended by death on April 18, 1873. Liebig was especially successful in giving a new form to chemical teaching, both in the laboratory and in his lectures, so that his pupils spoke of him all their lives with genuine enthusiasm. It is no wonder that in his time Giessen was the assembling-place of all scientific chemists, so that a great number of the most important investigators in the field of chemistry are to be reckoned among the pupils of Liebig. Of the most important of these there may here only be mentioned A. W. Hofmann, H. Kopp, Strecker, Fresenius, Varrentrapp, Muspratt, Gerhardt, Wurtz, Frankland, and Volhard. The individual researches of Liebig will have to be mentioned so frequently in the course of the general description of the work

of this period that a special account of them cannot be given here.

Friedrich Wöhler, born in 1800 at the village of Escherscheim, near Frankfurt am Main, at first studied medicine at Marburg and Heidelberg. Under the influence of L. Gmelin he soon turned to the study of chemistry, and was sent by him to Berzelius at Stockholm. In the autumn of 1824 he returned to Germany, where he acted as teacher of chemistry first at the city technical school in Berlin, and later at the technical school at Cassel. In the year 1836 he was made Professor of Chemistry at the University of Göttingen, where he was active till his death on September 23, 1882. He also, in addition to being a successful and fruitful original worker, was especially active as a teacher; and, like Liebig, he attracted to himself a number of pupils, so that the co-operation of these two distinguished men was of great influence for the future of chemistry in Germany. Among his pupils may be named especially Kolbe, Geuther, Limpricht, Fittig, and Beilstein.

J. B. A. Dumas was born at Alais in the year 1800. He was at first an apothecary, and while following that calling came to Geneva. In that town he met various chemists, and obtained from this intercourse much incitement to scientific study. In 1823 A. von Humboldt caused him to go to Paris, where he afterwards remained. In addition to his activity as Professor of Chemistry, he also occupied various dis-

tinguished positions in public life, becoming a Minister in 1848, and in 1868 perpetual secretary of the *Académie des Sciences.* He died in 1884 at Cannes. His important researches in physics and chemistry we have in part become acquainted with in the preceding chapter, but we shall also frequently meet with them in the more detailed account of this period.

Robert Wilhelm Bunsen, born on March 31, 1811, at Göttingen, became, after a short career as lecturer there, Wöhler's successor in Cassel. In 1838 he was made Professor at Marburg, then spent a short time at Breslau, and in 1858 became Professor at Heidelberg. He died at an advanced age in 1902. Bunsen, who began his scientific work with the researches upon cacodyl compounds, occupied himself later principally with physico-chemical problems, among which his investigations on spectrum analysis may be regarded as the most important scientific advance. By the naming of the German electro-chemical society the *Deutsche Bunsengesellschaft für Angewandte Physikalische Chemie* his name was for ever associated with physical chemistry.

Auguste Laurent, born in 1807 at La Folie, near Langers, was a pupil of Dumas. He was at first Professor at Bordeaux, and became in 1848 Warden of the Mint at Paris, where he died in 1853.

His friend, **Karl Gerhardt,** was born in 1816 at Strassburg. He studied at various German institutions, among others at Giessen under Liebig. He

afterwards worked for some years in Paris, became in 1844 Professor of Chemistry at Montpellier, in 1848 at Paris, and in 1855 at Strassburg, where he died in 1856.

C. A. Wurtz, born in 1817 at Strassburg, was a pupil of Liebig and Dumas. In 1845 he became Professor of Chemistry at various institutions in Paris. From 1866 to 1877 he was Dean of the Medical Faculty, and he died in Paris in 1884. In addition to carrying out splendid experimental investigations in organic chemistry, he also displayed successful literary activity, publishing, besides the *Dictionnaire de Chimie Pure et Appliquée,* the *Leçons de Philosophie Chimique* (1864), a *Traité Élémentaire de Chimie Médicale* (1864), and *La Théorie Atomique* (1879).

August Wilhelm von Hofmann was born at Giessen on April 3, 1818. It may very well have been Liebig's influence which caused him to turn to chemistry after several years of philosophical and legal studies. He was at first Liebig's assistant, then for a short time lecturer at Bonn, whence he was called in 1845 to the newly founded College of Chemistry in London. In 1864 he returned to Bonn, and in 1865 became the successor of Mitscherlich at the University of Berlin. He died on May 5, 1892. His numerous and very successful experimental investigations were chiefly concerned with organic substances containing nitrogen and phosphorus, and were of the most far-reaching import-

ance in the development of the coal-tar dye industry. He was the founder of the German Chemical Society (1868), which in recognition of his services preserved a lasting memorial to him by giving his name to the building erected by subscription in 1900 for the meetings of the society (the *Hofmannhaus*).

A. W. Williamson, a pupil of Liebig, was born in 1824. He was Professor of Chemistry at University College, London. His researches on the formation and constitution of the ethers are of especial importance.

August Kekulé, born September 7, 1829, at Darmstadt, was lecturer at Heidelberg from the year 1856, and became in 1858 Professor of Chemistry at Geneva, whence he moved to Bonn in 1865. Here he remained till his death on July 13, 1896. His researches, which were of fundamental importance for the theoretical views of organic chemistry, and also influenced the practical application of organic reactions, show him to have been one of the greatest of chemical investigators. Among the results of his literary activity, his text-book of organic chemistry deserves especial mention. A permanent and worthy memorial of him was furnished by his pupils and colleagues by the erection of a monument to him, which has found a place in front of the Chemical Department of the University of Bonn.

Hermann Kolbe, born in 1818 at Elliehausen, near Göttingen, studied from 1838 under Wöhler in

Göttingen. Between 1842 and 1847 he was partly in Marburg as Bunsen's assistant, partly in London with Lyon Playfair, and partly in Brunswick as editor of the *Dictionary of Chemistry*, founded by Liebig. In 1851 he became the successor of Bunsen at Marburg, and in 1865 accepted a call to Leipzig, where he was active till his death on November 25, 1884. For forty-two years he enriched chemistry with a series of striking researches of a theoretical and experimental nature. In regard to his literary activity, there should be especially mentioned, in addition to numerous essays for the above-mentioned dictionary, a comprehensive text-book of organic chemistry, which was followed later by a shorter one on inorganic and organic chemistry. From 1870 he also conducted the publication of the *Journal für praktische Chemie*, founded by Erdmann.

E. Frankland, born in 1825, worked at first in Germany under the direction of Liebig, Bunsen, and Kolbe, and became later Professor of Chemistry, first at Manchester, then in London. In addition to the discovery of the organo-metallic compounds, which have only recently attained great importance from the work of Grignard, his investigations made essential contributions to our ideas on the nature of the valency of the elements.

Isomerism and Chemical Constitution.

Wöhler's synthesis of urea, besides being a real organic synthesis, furnished in addition the most striking demonstration that two chemical compounds of similar quantitative composition may possess different properties, and be, therefore, two different substances. Various cases of this kind had already become known. As instances may be mentioned the various modifications of silica, the two forms of calcium carbonate, and fulminic acid, which was discovered by Liebig in 1819, and possesses the same composition as cyanic acid. But none of the examples known at that time was so striking as that of urea and ammonium cyanate, for the former is a decided base and the latter a well-defined salt. When Berzelius in 1830 found that the acid arising as a by-product in the preparation of tartaric acid has the same percentage composition as the latter, he took in hand (though at first slowly) the further treatment of this question. In spite of the scanty material which stood at his command, he was able to classify this phenomenon. He termed compounds isomeric which, although of the same percentage composition, possessed different properties, and distinguished two kinds of cases of this sort—those of polymerism and those of metamerism. Polymeric substances are those which have similar percentage composition, but different properties and different atomic weights (according to Berzelius); while metameric substances possess similar com-

position, different properties, and the same atomic weight. In the year 1841 he further separated isomerism in the case of elements from these isomeric phenomena, and termed it 'allotropy.' An example of allotropy is found in the case of carbon (diamond, graphite and amorphous).

Berzelius was further concerned to give himself some account of the cause of this phenomenon. From many indications in his work on the subject, it appears that he supposed a different placing of the atoms to be the probable cause of isomerism. He indicates, for instance, the difference between stannous sulphate and stannic sulphite, according to his mode of formulation, thus: $SnO+SO_3$ and SnO_2+SO_2. We are, however, in no way justified in supposing that Berzelius conceived the problem of the special arrangement of the atoms in the molecule in the form which, as a result of the development of organic chemistry, it now takes in modern stereochemistry. Nevertheless, the observation of isomerism in compounds, though perhaps it did not originate the inquiry into the constitution of chemical compounds, yet certainly brought it very much into the foreground. As early as the very year in which Wöhler prepared urea synthetically, Dumas and Boullay showed, in the course of a research upon alcohol and the ethers, that a certain atomic group, a so-called radicle, was peculiar to all these substances. They put their results together in a table from which their views on this point may be plainly seen, and they also indicate that these sub-

stances may be compared with the ammonium compounds :

Olefiant gas : C_4H_4.	Ammonia : NH_3.
Ethyl chloride : $C_4H_4 + HCl$.	Sal ammoniac : $NH_3 + HCl$.
Ether : $2C_4H_4 + H_2O$.	
Alcohol : $2C_4H_4 + 2\ H_2O$.	
Acetic ester : $2C_4H_4 + C_8H_6O_3 + H_2O$.	Ammonium acetate : $2NH_3 + C_8H_6O_3 + H_2O$.

Towards this view Berzelius adopted at first a very cautious attitude ; he speaks of it, for instance, in one place as 'a symbolical mode of expression which cannot be considered to represent the real constitution of the substances.' Later, however, he fell in with Dumas' views, and introduced the term 'etherin' for the radicle C_4H_4.

Theory of Radicles.

Here, therefore, we find the opinion maintained that to organic substances certain common atomic groups may be assigned, and that these play the same part as the elements do in inorganic compounds. A further advance in the assumption of such radicles was made by the memorable researches of Liebig and Wöhler on the radicle of benzoic acid. This work brought into general acceptance the view that organic compounds owe their properties to the radicles contained in them. The investigation fur-

nished such complete proof of the presence of the radicle benzoyl in a whole series of compounds, that the chemists of the time were convinced that the radicles proved to exist in such compounds were to be regarded as really existent groups of atoms, and that their isolation ought to be attempted. As alcohol and ether, and a series of compounds closely related to these two, were the most carefully investigated, they formed the principal material for the further development of the radicle theory. For its working out Berzelius and Liebig were chiefly responsible. The former endeavoured in 1833, with the help of his dualistic theory of inorganic compounds, to represent all organic substances also as possessing a binary composition. For this purpose he had to give up again the view which he had temporarily held as to the existence of radicles containing oxygen ; in order to avoid this, he regarded benzoyl as the oxide of the complex $C_{14}H_{10}$, and benzoic acid free from water as its peroxide. Ether is, according to this view, the suboxide of the radicle ethyl — he formulated it $(C_2H_5)_2O$—and alcohol he represented in the same way as the oxide of the radicle C_2H_6. We may see from this what difficulties his theory would encounter, for by this classification the very close relationship between ether and alcohol is not in any way expressed.

Liebig felt this inconvenience quite plainly, but in the endeavour to remove it he made a new mistake by arbitrarily ascribing to the radicles concerned

atomic weights twice as great as before. Ether he represented as the oxide of the radicle C_4H_{10}—*i.e.*, as $2(C_4H_{10}).O$—and alcohol as its hydroxide—*i.e.*, as $C_4H_{10}O.H_2O$—so comparing the former with potassium oxide, and the latter with potassium hydrate. The difference between the system of Liebig and that of Dumas lay, therefore, in the fact that Dumas represented ether as a hydrate ($2C_4H_4.H_2O$; *cf.* p. 150), while Liebig made it an oxide—$2(C_4H_{10}).O$. Dumas maintained his etherin theory for a long time in opposition to Liebig's views, but was unable to sustain it in the end, especially when the discovery of the mercaptans by Feise in 1834 gave Liebig a new opportunity to discuss the reasons for and against his theory. This publication appeared in 1836 in the *Annalen der Chemie und Pharmazie* ; he represented the mercaptans similarly to alcohol, as consisting of ethyl sulphide and hydrogen sulphide, and came to the conclusion that ether is not a hydrate, but an oxide. When finally Dumas gave up his etherin theory and joined Liebig in further investigations, the theory of radicles reached (towards the year 1837) its highest point. In Liebig's name Dumas makes a point of the comparison of the organic radicles with the elements, and in a paper which appeared in the *Comptes Rendus de l'Académie des Sciences* in Paris he designates organic chemistry as 'the chemistry of the compound radicles.' The passage reads : 'Organic chemistry has its own elements, which play the part sometimes of chlorine or of oxygen, sometimes of a metal. Cyanogen,

amidogen, benzoyl, the radicles of ammonia, of the fats, of alcohol and its derivatives form the real elements of organic nature, while the most simple constituents—carbon, hydrogen, oxygen, and nitrogen—first make their appearance when the organic matter is destroyed.'

In further working out the theory of radicles, the need arose of a somewhat more precise definition of the conception of a radicle; this was furnished by Liebig, who in 1838 characterized the radicle cyanogen in the following terms: 'We call cyanogen a radicle because—

'1. It is the unchanging constituent of a series of compounds; because

'2. It may be replaced in these compounds by other simple bodies; and because

'3. In its compounds with a simple substance the latter can be separated and replaced by equivalents of other simple substances.'

He further laid it down that a radicle was to be regarded as such if it fulfilled at least two of these conditions. This gave a stimulus to the careful investigation of the chemical behaviour of organic substances with special reference to their transformation and decomposition products. This it is mainly that we owe to the theory of radicles, in spite of the numerous errors into which it led chemists at the time. About the year 1850 the theory of radicles received considerable support from Bunsen's researches on the cacodyl compounds. This work showed that the product obtained by dis-

tilling arsenious acid with potassium acetate contained an arsenical radicle, which remained unchanged in a series of reactions, and, moreover—an especially valuable point for the current views—could be isolated. The radicle was named cacodyl, and the above product is consequently to be represented as its oxide, with the formula $C_4H_{12}AsO$.

THE PHENOMENA OF SUBSTITUTION.

Before we follow the course of the radicle theory further, we must concern ourselves with the study of some researches of Dumas, which also fall in the fourth decade of the last century. The occasion for these investigations was given by Gay-Lussac's discovery of the formation of cyanogen chloride from hydrocyanic acid, as well as the synthesis of hexachloroethane from ethylene chloride by Faraday, and the preparation of benzoyl chloride from benzaldehyde according to Liebig and Wöhler. The point of these researches is that in various organic compounds hydrogen can be replaced by other elements or radicles. These observations stand, however, in contradiction to the dualistic doctrine of Berzelius, because electro-positive hydrogen is replaced by the electro-negative elements chlorine, bromine, and iodine.

With the assistance of his own investigations of the year 1834 upon the action of chlorine upon oil of turpentine, and upon the formation of chloral from alcohol, Dumas obtained two rules by which

to express the facts of substitution (for which he proposed the term *metalepsie*), without putting forward any theory in connexion with it. The two rules are :

1. If a substance containing hydrogen be subjected to the dehydrogenating influence of chlorine, bromine, or iodine, it takes up for each atom of hydrogen which it loses an equal volume of chlorine, bromine, etc.

2. If the substance contain water, it loses the hydrogen corresponding to this without replacement.

While the former of these rules is intelligible as it stands, the latter requires a commentary. We must realize in particular that Dumas represented alcohol as a compound of ethylene and water (p. 150), and if we formulate this, the second rule in his paper should become clear :

$C_2H_4H_2O.$	$C_2Cl_3HO.$
Alcohol.	Chloral.

The facts set out in these two statements caused Dumas to undertake further experiments in this direction. He investigated, for instance, the oxidation of alcohol to acetic acid, and found that in this case every atom of hydrogen is replaced by half an atom of oxygen. This led him to make a change in the former of the two rules quoted above ; he now said :

'When a compound is subjected to the dehydrogenating action of a substance, it takes up an

amount of the latter equivalent to the hydrogen lost.'

By this change Dumas clearly indicated the difference between atom and equivalent, and in this point lies the great significance of his two rules.

Laurent went a step further in the treatment of substitution processes in endeavouring to compare the chemical nature of the substituted with that of the original compound. He found that some similarities are still present between them, and this led him in 1839 to state that in chlorine substitution, for example, the chlorine molecules occupy the space left vacant by the hydrogen molecules, and that therefore in the new compound the chlorine plays to a certain extent the same part that the hydrogen did in the original one.

The Theory of Nuclei and the Theory of Types.

The result of this view was for Laurent to suppose the existence of so-called 'nuclei' in organic compounds. He distinguished between primitive nuclei, composed of carbon and hydrogen in simple atomic proportions, and derived or secondary nuclei, arising either by substitution of the hydrogen by other elements or compound radicles such as amidogen or nitrile, or by addition of atoms. The theory of nuclei of Laurent differed from the radicle theory essentially in denying the unchangeableness of the radicles. Liebig and Berzelius in particular opposed

it most energetically. Unfortunately, the researches of Laurent contained, even in the experimental portions, so many omissions and inaccuracies that it was not difficult for his opponents to criticize it sharply. Liebig, in his review of the theory, even comes to the conclusion that it is unscientific and injurious. It was supported again, however, by the researches of Dumas upon chloracetic acid in 1839, for this work furnished definite proof that in the case considered a real analogy exists between the original substance and the substitution products. Dumas used these observations to build up his theory of types. Since acetic acid in which six atoms of hydrogen are replaced by six atoms of chlorine nevertheless remains a monobasic acid, and gives similarly constituted products with caustic potash, he concluded that in organic chemistry there are certain types which persist even when in place of hydrogen an equal volume of chlorine, bromine, or iodine is introduced. To the same chemical type are therefore to be ascribed acetic acid and trichloracetic acid, aldehyde, and chloral, as well as marsh-gas, chloroform, bromoform, and iodoform. A chemical type includes, in fact, compounds which contain the same number of equivalents combined in the same way. Dumas effected an extension of this conception of types by the introduction of the so-called 'mechanical type,' to which he assigned all compounds which can be imagined to be formed from each other by equivalent substitution, even though their properties be quite different. What

idea Dumas had of these types may be seen best from his statement that ‘alcohol, acetic acid, and chloracetic acid belong to the same natural family, acetic acid and chloracetic acid to the same species.’ It is therefore easily seen that the theory of types of Dumas closely follows the theory of nuclei of Laurent, and it may be considered certain that, although Dumas in his publications quotes Laurent in many places, in time many ideas due to Laurent came to be ascribed to Dumas, who enjoyed just at that time a great authority. It is worth mentioning further that Dumas also assumed the replaceability of carbon by other elements and compound groups: this he was led to do by Walter's experiments upon the action of sulphur trioxide on camphoric acid, in which were obtained a sulpho-camphoric acid and carbon monoxide. Although this hypothesis met at the time with the most vigorous opposition, time has shown that Dumas was not wrong.

The most important consequence which was to be drawn from the theory of types was the desire for a monistic system, and so Dumas directed himself with energy against the dualistic theory, which for twenty years had suffered no attack. He did not in any way deny the influence of electrical forces in chemical reactions, but that the electrical condition of the atoms should be unchangeable he considered to be irreconcilable with the phenomena of substitution, and therefore wrong.

His position towards dualism may be expressed thus: ‘Every chemical compound forms a separate

unit, and does not therefore consist of two parts; its chemical character depends chiefly upon the arrangement and number of the atoms, and only to a subordinate degree upon their chemical nature.' It was not easy for Berzelius to maintain his dualistic system under these circumstances. First he rejected the possibility of radicles containing oxygen and sulphur, allowing only those which contain carbon, nitrogen, and hydrogen. In this way he compared benzoyl with manganese dioxide, benzoic acid with manganic acid, thus:

$C_{14}H_{10}O_2$.	MnO_2.
$C_{14}H_{10}O_3$.	MnO_3.
$C_{14}H_{10}$.	Mn.

Chloracetic acid was then represented as a compound of oxalic acid and carbon chloride, or, as he termed it, an oxalic acid conjugated with C_2Cl_6:

$$C_2Cl_6 + C_2O_3\ ;$$

and acetic acid as the trioxide of the radicle acetyl, C_4H_6—*i.e.*, as $C_4H_6 + O_3$—so that in the year 1840 he still denied the existence of any similarity between the two acids. When in 1842 Melsens succeeded in turning chloracetic acid back again into acetic acid by the action of potassium amalgam, he termed acetic acid a conjugated oxalic acid, whose conjunct is C_2H_6. This conjunct C_2H_6 was converted into C_2Cl_6 by the action of chlorine upon acetic acid:

$C_2H_6 + C_2O_3HO$ Acetic acid.
$C_2Cl_6 + C_2O_3HO$ Chloracetic acid.

Here Berzelius expressed nothing else than the possibility of a substitution within a so-called conjunct. It is therefore easy to see that even with this assumption of conjuncts an extension of the electrochemical theory to organic chemistry was impossible, because it did not agree with observation. As a result of this, the followers of dualism became less and less numerous, and in 1844 Liebig began openly to oppose these speculations of Berzelius. The work which was mainly instrumental in causing Liebig to incline to the monistic view was A. W. Hofmann's investigation in the laboratory at Giessen of the chlorine and bromine derivatives of aniline. This research showed that the chemical character of a substance is dependent to no small extent upon the arrangement of the atoms. On the whole, it is noticeable at this period that the greater number of chemists turned their attention more and more away from the theoretical considerations of organic chemistry to the other departments of chemistry. A change in this respect did not occur until Laurent, in conjunction with Gerhardt, attempted a unification of the theory of radicles and the theory of types. This theory is termed, to distinguish it from that of Dumas, 'the later theory of types.' To begin with, Gerhardt denies the preexistence of water in most organic compounds, and finds no grounds for the assumption that the substances produced in a reaction are already contained in the reacting substances, as was frequently supposed at that time. He points out, on the contrary,

that there is a class of compounds which are formed in almost every organic decomposition, although the substances decomposed cannot be reconstructed from them. Such substances are of simple composition, but of extraordinary stability, such as water, carbon dioxide, hydrochloric acid, and ammonia. Gerhardt was led to these conclusions chiefly by the investigation of the formation of nitrobenzene from benzene and nitric acid, which had already been observed by Mitscherlich. He even speaks on this subject as follows : 'When two substances react on one another, one of them loses an element (hydrogen), which unites with an element (oxygen) from the other to form a stable compound (water), and then the "residues" unite with one another. In the case of nitrobenzene, the benzene yields the hydrogen and the nitric acid the oxygen necessary to form water, and so nitrobenzene is in some sense a compound of two radicles—the residue of the benzene and the residue of the nitric acid.'

By the term 'residues,' accordingly, he understood atomic complexes which, on account of the stronger affinity of the single elements for one another, remain over when two substances react, and unite with one another. This theory is termed the theory of residues. Gerhardt represented the residues, however, not as real groups of atoms actually present in compounds ; they existed there in a 'substitution form' different from that of compounds of similar composition in the free state. As an ex-

ample, the action of sulphuric acid on benzene may serve; the SO_3 residue produced is not identical with the SO_3 in lead sulphite, but is in the so-called substitution form. The nitrobenzene reaction also lead him to the determination of the basicity of acids. For in this case there is formed from monobasic nitric acid a neutral compound, nitrobenzene, while by acting with dibasic sulphuric acid upon alcohol, monobasic ethylsulphuric acid is obtained. These facts led Gerhardt to state the following law: The basicity of a conjugated compound is equal to the sum of the basicities of the conjugating substances minus one. This rendered it possible to determine the saturation-capacity of the acids, and so he was able to indicate acetic acid, as well as hydrochloric and nitric acids, as monobasic, sulphuric acid and oxalic acid as dibasic.

Of particularly great influence on the further development of the views as to the constitution of organic compounds were Williamson's researches upon the action of ethyl iodide on potassium ethylate; they were undertaken in the hope of obtaining alcohol, but instead of this ether was produced. The most simple and plausible explanation of this result was furnished by the derivation of alcohol and ether from water, which was published by Laurent in 1846. Laurent expressed this in a table, in which he at the same time also compared these substances with the alkalis.

HHO.	EtHO.	EtEtO.	KHO.	KKO.
Water.	Alcohol.	Ether.	Potassium hydrate.	Potassium oxide.

Williamson was consequently able to formulate as follows the reaction discovered by him :

$$\begin{matrix}C_2H_5\\K\end{matrix}O + C_2H_5I = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}O + KI.$$

The researches in which he followed up this reaction contributed still further to strengthen these opinions. By the action of methyl iodide on potassium ethylate he obtained ethylmethylether, and he was able to obtain the same compound from potassium methylate and ethyl iodide :

$$\begin{matrix}C_2H_5\\K\end{matrix}O + CH_3I = \begin{matrix}C_2H_5\\CH_3\end{matrix}O + KI.$$

$$\begin{matrix}CH_3\\K\end{matrix}O + C_2H_5I = \begin{matrix}C_2H_5\\CH_3\end{matrix}O + KI.$$

These results further gave occasion for a thorough investigation of the formation of ether from alcohol and sulphuric acid, which had often attracted attention before, and had been explained as being due to the dehydrating action of the sulphuric acid. Liebig now showed that the formation of ethylsulphuric acid preceded the production of ether, so that the sulphuric acid did not withdraw water from the alcohol, but ether, which united with the sulphuric acid to form ethylsulphuric acid, and this substance then decomposed at a temperature of 120-140° into sulphuric acid and ether. Berzelius, however, did not agree to this explanation, and endeavoured to maintain, on the contrary, that the sulphuric acid did not take part in the reaction, but was only a 'contact-substance,' and that therefore

the action takes place as a result of its catalytic power.

In the year 1850 it was further shown by Graham that ethylsulphuric acid only gives rise to ether when alcohol is present, and that it is decomposed by water into alcohol and sulphuric acid. Williamson explained the former reaction by the equation

$$\begin{matrix}C_2H_5\\H\end{matrix}SO_4 + \begin{matrix}C_2H_5\\H\end{matrix}O = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}O + \begin{matrix}H\\H\end{matrix}SO_4.$$

Williamson's views found confirmation from the production of ethylamylether from ethylsulphuric acid and amyl alcohol, and from several other syntheses of these so-called 'mixed ethers.' The comparison of organic substances with water is, as Williamson says, of great use in the examination of chemical reactions, since it simplifies our views and lays down a common basis for comparison.

By acting with potassium hydrate on cyanic esters, Wurtz, in 1849, obtained substances bearing a remarkable likeness to ammonia, and he derived these from ammonia in the same way as Laurent and Williamson had derived alcohol and ether from water. These compounds are, in fact, ammonia in which hydrogen is replaced by the radicles methyl, ethyl, etc. A. W. Hofmann arrived at the same compounds by treating the alkyl iodides with ammonia, and so furnished no inconsiderable confirmation of the views of Wurtz. The result of these researches was, as Wurtz expressed it, the introduction of ammonia as a 'type.'

By means of the reaction which led Wurtz to the formation of substituted ammonias, Williamson in 1851 was able to prove that the dibasic acids depend upon the presence of polybasic radicles. He formulated the Wurtz reaction as follows :

$$\begin{matrix}K_2\\H_2\end{matrix}O_2 + \begin{matrix}C_2H_5\\CN\end{matrix}O = \begin{matrix}K_2\\CO\end{matrix}O_2 + \begin{matrix}C_2H_5\\N\end{matrix}H_2,$$

and speaks of it thus : 'The atom CO is equivalent to two hydrogen atoms ; when it replaces them it holds together two atoms of potassium hydrate in which the hydrogen was contained, and so there necessarily arises a dibasic compound, potassium carbonate.' In this way he explained the production of oxamide from the dibasic radicle C_2O_4, and was able to isolate, in addition to sulphuryl chloride (already obtained by Regnault from sulphur dioxide and chlorine), chlorsulphonic acid, which he prepared by acting upon sulphuric acid with phosphorus chloride. As a result of the latter experiments he represented sulphuric acid as a dibasic acid, and was also able to disprove Gerhardt's view that formation of anhydride must always precede formation of chloride in the case of a dibasic acid.

Gerhardt's Classification.

Gerhardt now took up an observation made by Schiel in 1842, that the alcohol radicles form a series the separate members of which always differ by $n\mathrm{CH}_2$. He called substances which differ by $n\mathrm{CH}_2$

'homologous,' and showed that they all display great chemical similarity, while, according to the researches of Kopp, their physical properties slowly but continuously change. 'Isologous' are, according to Gerhardt, compounds which possess similar chemical properties, but do not differ from each other by nCH_2. Instances are acetic acid and benzoic acid. 'Heterologous' he termed compounds which might be formed from each other by simple reactions, and are therefore related by their mode of formation, though chemically different.

This is the fundamental idea of Gerhardt's classification of organic compounds. He himself compares this arrangement very aptly with a pack of cards laid out according to the colour and value of the separate cards. Every card that is wanting is determined in colour and value by its position; and so also the wanting members of a chemical series can be described beforehand in respect of principal properties—origin, decomposition, etc.

The members of all heterologous, homologous, and isologous groups he referred to the four primitive types: water, hydrochloric acid, hydrogen, and ammonia. It may be added for the sake of example that he assigned to the water-type all alcohols, ethers, acids, anhydrides, aldehydes, and ketones.

In this way radicles were introduced into the mechanical types of Regnault and Dumas, certainly in Gerhardt's sense of the term, for he had defined this conception as early as 1839, declaring radicles

to be residues of compounds which in certain reactions could be transferred without decomposition from one substance to another. They were not, therefore, necessarily capable of independent existence, but only expressed the relations according to which elements or groups of atoms can naturally replace one another. Gerhardt further pointed out that the symbols obtained do not represent the real arrangement of the atoms themselves; he considered it to be impossible to determine the true constitution of substances, and it was probably in this respect that Gerhardt's classification appeared wanting to the chemists of the time. It probably owed its general acceptance to reasons of convenience, as Liebig pointedly says when he speaks of its 'usefulness.'

Atom, Molecule, and Equivalent.

Before we concern ourselves further with the fate of the theory of types and of Gerhardt's classification, and with their passage into structural chemistry, it is necessary to deal with some opinions on the conceptions 'atom,' 'molecule,' and 'equivalent,' expressed by Gerhardt and Laurent between the years 1840 and 1850. We have seen in the preceding chapter with what good fortune Berzelius determined the relative atomic weights of the different elements. About the year 1840 the whole system which had grown out of this work threatened, under the influence of Gmelin and his school, to

be forsaken. Efforts were made to replace the atomic weights of Berzelius by so-called combining weights (also termed 'equivalents'), which were to be the values expressing the simplest proportions of the reacting substances. The result of this was to cause most of the values given by Berzelius to be halved, so that numbers like $C = 6$, $O = 8$, etc., were introduced. Then in 1842 Gerhardt pointed out that the quantities of water, carbon dioxide, etc., produced in organic reactions never correspond to one equivalent, but always to a multiple of it, usually two. If, therefore, the symbols H_2O_2, C_2O_4 in the system of Gmelin indicate one equivalent, then the formulæ of all inorganic compounds must be doubled, while if they correspond to two equivalents a halving of the organic formulæ must be resorted to. Gerhardt sought to abolish this contradiction by deciding in favour of the atomic weights of Berzelius ($H = 1$, $C = 12$, $O = 16$). A complete extension of his views Gerhardt was not able to effect; this was chiefly due to the fact that he wrote the metallic oxides Me_2O, referring them to the water-type, while Berzelius represented them as MeO. As a result of this, he ascribed to a number of elements, such as calcium, lead, etc., values half as great as those of Berzelius—*e.g.*, $Ca = 20$, $Pb = 103{\cdot}5$. As Gerhardt also termed these numbers equivalents, much confusion was created in this direction, and was only removed later by considerations advanced in conjunction with Laurent. The latter pointed out in a decisive manner that the equivalents of elements

of Gerhardt are not at all comparable with those of the compounds. He made it clear that the former were the atomic weights of the elements, and the latter the molecular weights of the compounds, and understood by the term 'molecular weight' the weight (either of an element or of a compound) which under similar physical conditions occupies the same volume as two atoms of hydrogen. In this way he obtained for chlorine the formula Cl_2, for oxygen O_2, for nitrogen N_2, etc. In general, he defined a molecule as the smallest quantity which must be employed to bring a compound into existence. By the term 'atom' he understood, on the contrary, the smallest quantity of an element which occurs in compound substances. As atomic weights, there came into consideration, therefore, the values of Gerhardt and Berzelius. The equivalents, on the contrary, he conceived as equivalent quantities of analogous substances, and he laid especial emphasis on the point that one and the same element can possess different equivalents.

These views, however, found at the time but slight recognition; the combining weights of Gmelin were for the most part adhered to, so that even Gerhardt himself, in his text-book of 1853, still employed equivalent formulæ for the sake of generality. Full light was first brought into this confusion through the efforts of the Italian chemist Stanislaus Cannizaro, who strove for the acceptance of the atomic weights obtained from the vapour densities, and in the case of the metals assumed, in opposition

to Gerhardt, the values calculated from their specific heats.

We may now turn back again to Gerhardt's classification of organic compounds. We have already seen that the chief point in its favour was its convenience, but that it could not long satisfy chemists, since in no way did it furnish any conclusion as to the constitution of the substances concerned. In an extension of it in this direction Frankland and Kolbe took the greatest share. Kolbe sought to revive the views of Berzelius, and took up again the idea of conjuncts, probably on account of his synthesis of trichloracetic acid by acting upon betrachlorethylene in sunlight in the presence of water. He formulates it, like Berzelius, as a conjugated oxalic acid—$C_2Cl_6 + C_2O_3 + HO$ (*cf.* p. 159). In addition, both Kolbe and Frankland understood radicles in the old sense of the term, not in Gerhardt's, and from this are derived the researches upon the electrolysis of organic acids, in which Kolbe was led by the idea of splitting acetic acid into the conjuncts, methyl and oxalic acid, ascribed to it. To these researches belong (1844-1850) the preparation of methyl cyanide from ammonium acetate and phosphoric anhydride by Dumas, the saponification of the nitriles by Frankland and Kolbe, and the isolation of ethyl from ethyl iodide by means of zinc by Frankland. They were all utilized by Kolbe to rehabilitate the theory of conjuncts. He termed, for instance, cacodyl, methyl conjugated with arsenic, $AsCH_3$ ($C=6$); acetic acid, $(C_2H_5)C_2O_3.HO$; alde-

hyde, $(C_2H_5)\widehat{\ }C_2O.HO$, etc. This formulation certainly had the advantage that, as Kolbe himself pointed out, the four carbon equivalents of acetic acid are not of equal value, two being contained in it as methyl, while the other two form the point of attachment for the affinity of the oxygen.

VALENCY.

In 1852 Frankland attacked Kolbe's principle, according to which the conjugating radicle is of subordinate importance in determining the nature of the compound, and was also able to convince him that this view was untenable. Frankland showed that arsenic in the free state could combine with five atoms of oxygen, but as cacodyl, on the contrary, only with three atoms ; he described this by saying that arsenic, in conjugating with methyl, changes its saturation-capacity. He then carried over the results obtained in these investigations, and in those on tin ethyl and antimony ethyl, to the inorganic compounds of nitrogen, phosphorus, arsenic, and antimony. He found that these elements, in forming compounds, show a tendency to unite either with three or with five equivalents of other elements. The ratio 1 : 3 occurs in the case of—

NO_3, NH_3, NI_3, NS_3,
PO_3, PH_3, PCl_3,
SbO_3, SbH_3, $SbCl_3$,
AsO_3, AsH_3, $AsCl_3$,

and the ratio 1 : 5 in—

$$\begin{array}{lll} NO_5, & NH_4O, & NH_4I. \\ PO_5, & & PH_4I. \end{array}$$

It is sufficiently clear from this, as Frankland himself says (*Ann. der Chem.*, **85**, 368), that a regularity of this kind obtains, and that the affinity of the combining atoms of the above-named elements is always satisfied by the same number of atoms entering into combination, without regard to their chemical character. In the same paper he further says, declaring himself in favour of a fusion of the theory of types with the electro-chemical theory of radicles : 'For while it is clear that certain types of series of compounds do exist, it is, on the other hand, also clear that the nature of a substance derived from the original type depends considerably upon the electro-chemical character of the separate atoms contained in it, and not solely upon the relative position of these atoms.' Here Frankland has really given up the idea of conjugation, and accepted the theory of types, though certainly in a somewhat altered form.

Kolbe, in 1857, expressed his agreement with Frankland's views, but strove to extend them further. He endeavoured to represent organic compounds entirely as derivatives of inorganic compounds, to some extent as arising from them by simple substitution ; for he derived all carbon compounds from carbonic acid, all sulphur compounds from sulphuric acid.

In Frankland's papers there is ascribed to the elementary atoms a varying but none the less always definite saturation-capacity, and this view contains the fundamental idea of the doctrine of valency. Although the latter is derived directly from Frankland's researches, yet it would nevertheless be justifiable to say that the doctrine of valency would have arisen without these researches, for it is a consequence of the separation of atom and equivalent. If the atoms are not of equal value, the question must arise as to what relation they bear to one another, and that is the question of valency.

What is remarkable about the origin of the doctrine of valency in general is that it required the investigation of such complicated substances as organic compounds, in order to bring into notice phenomena which are much more obvious among simple inorganic substances.* Analogously the special valency relations in the case of carbon were not discovered in the simplest way, as it is indicated by the two compounds CO and CO_2. Here, also, investigations of complicated compounds were necessary before an insight into these relations was obtained. To this subject belong the researches of Ray† upon the tribasic formic ester, those of Berthollet‡ upon glycerine, and those of Buff§ upon

* E. von Meyer, *Geschichte der Chemie*, 1905, p. 287.

† *Journ. Chem. Soc.*, **7**, 224.

‡ *Ann. de Chim. et de Phys.* [3], **41**, 319

§ *Ann. der Chem.*, **96**, 302.

ethylene, together with those of Wurtz* upon glycol, inwhich they found extension. A special description of them here would lead too far.

Structural Formulæ.

In 1857 Kekulé derived all compounds of the methyl series from the type hydrogen methyl—for example :

C_2H_4.	C_2H_3Cl.	C_2HCl_3.
Hydrogen methyl.	Methyl chloride.	Chloroform.

etc. With this is connected further work of Kekulé, which he put together in a paper, published in the *Annalen der Chemie* in 1858, entitled 'On the Constitution and Metamorphoses of Chemical Compounds and on the Chemical Nature of Carbon.' By these considerations he made it possible to extend the type 'methyl' to all carbon compounds, and so called into being a new system of organic chemistry. Starting from Frankland's researches on nitrogen and phosphorus, he applied the views developed by the latter in this connexion to the case of carbon, and so arrived at the tetravalence of carbon. He established this in the following words : 'If one considers the simplest compounds of this element, CH_4, CH_3Cl, CCl_4, $CHCl_3$, $COCl_2$, CO_2, CS_2, and CNH, it becomes obvious that the quantity of carbon which chemists have regarded as the least possible, as the atom, is always united with four atoms of a

* *Comptes Rendus,* **43**, 199.

monatomic or two of a diatomic element, that in general the sum of the chemical units of the elements combined with an atom of carbon is equal to four. This leads to the view that carbon is tetratomic.' Similar ideas had already been expressed by Kolbe and Frankland, so that it is not justifiable to ascribe to Kekulé the introduction of the conception of atomicity into chemistry. He himself also spoke in a very reserved manner of his views in this connexion, so that it is rather his followers who have unjustifiably exalted Kekulé's share in the matter. His service to chemistry is more to be sought in the fact that, by reason of the elementary saturation-capacity, he arrived at the idea that the elementary atoms in general are united to a varying degree among themselves, and that an exchange, and consequently a destruction, of single affinities occurs. Applying these views to the compounds of carbon, he showed that in the case of substances containing several atoms of carbon it must be supposed that some, at least, of the atoms are held by the carbon affinity, so that the carbon atoms themselves are united to each other by means of a portion of the affinity of one atom, and an equal amount of the affinity of another in each case. In this way he gave expression to the doctrine of the linkage of atoms in chains. He writes on this point as follows :* 'The simplest and therefore the most probable instance of such a union of two carbon atoms is that in which one affinity of one atom is united with

* *Ann. der Chem.*, **106**, 154.

one of the other. Of the 2×4 units of affinity of the two carbon atoms, two are therefore employed in holding together the two atoms ; there remain consequently six others which can be satisfied by atoms of other elements.' These views were still capable of much extension ; Kekulé also speaks, for instance, of a closer union of the carbon atoms in benzene and naphthalene, as well as of the case when two units of affinity are mutually satisfied, and of the relations in which other elements unite with carbon atoms. Independently of Kekulé, Couper* arrived at similar views, and he introduced also the use of a line to indicate the elements united with one another, thereby laying the basis for structural formulæ. The term ' structure ' is due to Butlerow,† though he erroneously meant by it the real arrangement of the atoms.

Various organic acids were closely investigated by Kolbe and Wurtz, on the basis of the tetratomicity of carbon. It was the researches on some oxyacids, such as glycollic acid and lactic acid, which led Wurtz to distinguish between atomicity and basicity. The former he described as conditioned by the valency of the radicle concerned, the latter by the number of hydrogen atoms replaceable by a metal. Further light was thrown upon this question by Kekulé in his text-book (1861), in which he says that lactic acid contains two typical hydrogen atoms—*i.e.*, hydrogen atoms united to carbon by

* *Comptes Rendus*, **46,** 1157 ; *Ann. Chim. et Phys.* [3], **53, 469.**

† *Ztschr. f. Chem.*, **1861, 553.**

means of oxygen. The two atoms are, however, different in properties, for one of them, like the typical hydrogen in acetic acid, is influenced by two oxygen atoms, while the other plays a part similar to that of the typical hydrogen in alcohol.

In the year 1862 Friedel obtained from acetone a propyl alcohol identical with that obtained by Berthelot from propylene. This Kolbe regarded as one of his isomeric alcohols, the possible existence of which he had prophesied in 1859, and he ascribed to it the formula

$$\left.\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right\} C_2O,OH.$$

This formulation received confirmation from the fact that this isomeric alcohol yielded acetone on oxidation. The amylene hydrate, discovered by Wurtz in 1862, and also termed by Kolbe an isomeric—that is, secondary—alcohol, was first recognized as a tertiary alcohol by Wischnegradsky in the year 1879. Kolbe in 1864 compared the alcohols with the amines, and so arrived at the following formulæ for them :

$\left.\begin{matrix} C_2H_3 \\ H \\ H \end{matrix}\right\} C_2,O,HO.$	$\left.\begin{matrix} C_2H_3 \\ C_2H_3 \\ H \end{matrix}\right\} C_2,O,HO.$	$\left.\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \end{matrix}\right\} C_2,O,HO.$
Simply methylated methyl alcohol.	Doubly methylated methyl alcohol.	Triply methylated methyl alcohol.

By the action of oxalic ester on zinc ethyl Frankland obtained an acid which Kolbe represented as a diethyloxyacetic acid, corresponding to the formula

$$C_2\left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ O_2H \end{matrix}\right\} C_2O_2,O,OH.$$

Kolbe further succeeded in obtaining an isobutyric acid, as well as three isomers of the formula of valerianic acid. Geuther in 1864 discovered aceto-acetic ester, which through the work of Frankland and Duppa, and later of J. Wislicenus, became the starting-point for numerous syntheses of organic acids, by which our knowledge of the acids in general, and of isomerism in particular, was rendered much clearer. By all these researches scientific organic chemists were continually being more incited to seek an explanation of the phenomena of isomerism; for the attempt to give the simplest possible form to these numerous cases, the so-called structural formulæ, developed with the help of the lines proposed by Couper, offered many advantages, and found accordingly more and more extensive use. It was easy to represent in this way the mutual relations of the separate atoms—*i.e.*, their mode of union. Although some important chemists like Butlerow and Kolbe fell into the error of thinking that by help of these formulæ the actual spacial arrangement of the atoms themselves could be expressed, yet this was not the general view. On the contrary, objections to such an idea were raised from various quarters. Nevertheless, this view gave rise to such notions as that the smallest particles of the elements were provided with little hooks in which the hooks of others became fixed (Naquet and Baeyer).

At the beginning of this chapter it has been mentioned that Berzelius recognized racemic acid as a

compound isomeric with tartaric acid. In the years 1860 and 1861 Pasteur investigated more closely this instance of isomerism, and found that there are four isomeric tartaric acids. Two of these show a peculiar behaviour towards polarized light, for they rotate the plane of polarization through the same angle, but in opposite directions. Pasteur further found that a mixture of the two in equal amounts produced racemic acid, which did not rotate the plane of polarization, and that it is possible by suitable means to split up racemic acid in its two 'optically active' components. Similar cases were also observed with other substances—for instance, amyl alcohol, aspartic acid, etc. Carius introduced for this kind of isomerism the term 'physical isomerism.' In 1875 Le Bel and van't Hoff sought to explain this isomerism with the aid of the atomic theory by referring the phenomenon of optical activity to the presence of a so-called 'asymmetric carbon-atom'—*i.e.*, one having its four valencies united to four different elements or groups of atoms.

We see, therefore, that the whole complicated structure of organic chemistry may be nevertheless built up in a comparatively simple way by assuming the tetravalency of carbon, and it was the natural endeavour of the chemists of that time to apply to inorganic chemistry also a view which had shown itself so fruitful in the department of organic chemistry. Here difficulties were soon met with, however, because the elements showed a varying

valency. As an example may be cited ammonia, in which the nitrogen only claims three units of affinity, and ammonium chloride, in which it claims five. Some chemists ascribed to the elements a so-called 'maximum saturation-capacity'; so that every element is provided with a definite number of points of affinity, of which in many cases only part are combined with other elements. Kekulé, however, resolutely opposed these views. He considered the atomicity of the elements as a fundamental property of the atoms, which would be as unchangeable as the atomic weights. Nitrogen he supposed trivalent, the halogens monovalent, and carbon tetravalent. In order to extend these suppositions completely he had to have resort to new hypotheses, and from these arose his classification of chemical compounds as atomic compounds and molecular compounds, and he was forced to suppose that in the latter the components were held together by forces different from those in the former. He expressed this in formulation by writing the two components separately—for instance:

Phosphorus pentachloride, $PCl_3.Cl_2$;
Ammonium chloride, $NCl_3.HCl$.

The especial characteristic of atomic compounds was, according to Kekulé, that they should be capable of assuming the gaseous condition without decomposing, while molecular compounds split up on heating in the manner indicated in their formulæ. Such a classification became untenable when it had

been observed (apart from a number of other exceptions) that phosphorus pentafluoride remained undecomposed in the gaseous state ; and so, towards the end of this period, most chemists must have been persuaded that the saturation-capacity of the atoms did vary under certain conditions.

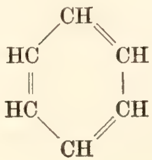
Mention ought also to be made here of various researches which were carried out at this time, and which were occupied with the question of the equivalence of the four affinities of carbon. The investigations referred to seem to have decided the question in the affirmative.

Although the constitution of a great number of organic compounds may be explained in a comparatively easy and simple way by supposing that the individual carbon atoms saturate one another, and so form a sort of 'carbon chain,' yet even Kekulé found that it is not possible to subject all organic substances to this assumption. In this connexion especially the compounds poor in hydrogen caused considerable difficulty.

Kolbe, Couper, and Wurtz gave it as their opinion that in ethylene or in acrylic acid one or more carbon atoms must be supposed to be trivalent, while Kekulé gave the preference to a double, or in other cases triple, binding of the separate carbon atoms. Later, however, he dropped this view, and expressed himself to the effect that the affinities of the individual carbon atoms were not fully saturated. In fact, on the whole, this question as to the constitution of such compounds is even now

not quite satisfactorily settled, though the general inclination is to the idea of a multiple linkage as expressed in the common terms 'double bond' and 'triple bond.' Still greater difficulties for the question of constitution were furnished by benzene and its derivatives. Kekulé first showed that benzene is the mother-substance of all those compounds which, on account of their connexion with some strongly smelling oils, are termed 'aromatic,' as opposed to the other organic compounds which, by reason of their relations with the fats, are termed 'aliphatic' or fatty substances.

Kekulé, who, as has already been stated, spoke of a closer binding of the carbon atoms in benzene and naphthalene, solved the question as to the constitution of benzene in a very fortunate way. Premising the tetravalency of carbon and the monovalency of hydrogen, he assumed in these compounds a linkage of the carbon atoms not in a simple chain, but so that they close to form a ring in which they are united three times by one valency each and three times by two. By this formula he could explain the non-existence of isomeric monosubstitution products of benzene, as well as the non-existence of more than three bi- and three trisubstitution products :



It was certainly soon pointed out from various quarters that, according to Kekulé's formula, the existence of four bi-substitution products must be possible. The results of such considerations were proposals to alter Kekulé's formula, as evidenced by the prism formula of Ladenburg, the diagonal formula of Claus, the centric formula of Baeyer, and the quinone formula of Dewar. To strengthen his view, Kekulé then made a further hypothesis, in which he assumes an oscillation of the fourth carbon valency between the carbon atoms, so that each two carbon atoms are sometimes singly, sometimes doubly, bound. In general, one finds the formula of Baeyer and that of Kekulé most frequently employed. In this way the difference between the fatty substances and the aromatic compounds is laid down: in the former the carbon atoms are united with each other in the form of an open chain, in the latter in the form of a ring.

The successful explanation of so many peculiarities of the benzene derivatives by means of Kekulé's idea of the ring formula led to the assumption of similar rings in various other compounds, not only in those consisting only of carbon and hydrogen, but in those containing nitrogen, sulphur, or oxygen as well. The benzene formula was followed by that of naphthalene by Erlenmeyer, then by that of pyridine by Dewar (1871) and Körner, and that of quinoline by Dewar (1871). To these followed thiophene, furane, and pyrrole, in which the ring is to be formed not from six, but from five

atoms. In course of time compounds were also obtained in which only three or four atoms take part in the ring formation, as in the case of trimethylene (Freund, 1882) and of the derivatives of tetramethylene and pentamethylene.

These views led to a close study of isomerism among organic compounds, and these phenomena proved to be especially interesting in the case of benzene and its derivatives. Kekulé at an early date suggested the idea of determining the 'position' of substituting groups, and the subject found successful treatment in the researches of Baeyer, Graebe, Ladenburg, and others.

Vapour Densities.

We have already seen (p. 126) that the method of determining vapour densities discovered by Dumas exercised a great influence on the determination of the atomic weights. It is, therefore, not remarkable that the need had made itself felt of simplifying and improving this method as much as possible. Dumas in his method determined directly the weight of a given volume of the vapour. Gay-Lussac, and later A. W. Hofmann (1868), changed the principle of the experiment by measuring the gaseous volume occupied by a weighed quantity of the substance to be investigated. In 1878 this method was again altered by V. Meyer. He carried out the determination by measuring the volume of air or other indifferent gas which was

displaced by the substance under investigation when it is turned into vapour. This method rendered it possible to determine vapour densities at various temperatures by correspondingly changing the liquid used in the heating-bath—water, sulphur, nitrobenzene, etc. In this way it was found that iodine is monatomic at a temperature of 1,700°; that aluminium chloride corresponds at low temperatures to the formula Al_2Cl_6, at higher temperatures to the formula $AlCl_3$; and that to mercurous chloride in the form of vapour the formula HgCl is to be ascribed. These observations had considerable significance for the doctrine of valency.

Spectrum Analysis.

Even during the phlogistic period the observation was made by Marggraf and Scheele that sodium compounds, for instance, impart to the flame an intense yellow colour. Later, we find close investigations of the spectra of many coloured flames. There may be mentioned here the researches of John Herschel (1822), Fox Talbot (1826), W. A. Miller (1845), and Swan (1856); and in addition the spectra of electric sparks were investigated by Frauenhofer, Wollaston, Wheatstone, Angström, and others. In all these researches, however, the question was always left out of consideration as to whether the bright lines of an incandescent gas are conditioned by its individual chemical constituents. This question was first answered in 1859 by Kirch-

hoff and Bunsen, who found that the bright lines of an incandescent gas do depend on its chemical constituents. The second statement made by them, that the manner of combination, the temperature, and the pressure are without influence, experienced in the course of time many limitations, which were made by Roscoe and Clifton, Mitscherlich, and others. As a result of the work of Bunsen and Kirchhoff, it was possible to develop an analytical method from the phenomenon of the bright lines of a spectrum, and this method brilliantly showed its extraordinary fruitfulness in the discovery of new elements (*cf.* p. 190). The close investigation of the solar spectrum, in conjunction with the other observations, permitted the solution of the question as to what elements are contained in the sun. In connexion with this matter, besides Kirchhoff and others, Müller and Kempf (1886), Rowland (1881-1888), and Thalén deserve especial mention.

The Periodic System.

Before we concern ourselves with the historical development of the individual branches of chemistry which rapidly grew under the influence of the theoretical speculations previously described, we must consider some advances in the theoretical views of inorganic chemistry. The English chemist Newlands and the German chemist Lothar Meyer arranged the elements in a series in the order of their atomic weights, and they found that, after a

certain period, the physical and chemical properties of the elements concerned showed great similarity, so that the elements can be divided in this way into natural groups. Although this attempt did not at first find much recognition, yet it took comprehensible shape in the year 1869 through extensions of it by L. Meyer and Mendeléeff, due to many new and accurate determinations of the atomic weights. The fruit of these researches was the establishment of the so-called periodic system of the elements, which gives expression to the fact that the properties of the elements are periodic functions of their atomic weights. By its help Mendeléeff was enabled to predict, by filling up existing gaps, the existence of unknown elements, and even the approximate value of their atomic weights. The success which crowned these speculations is shown by the fulfilment of such prophecies in the discovery of germanium, gallium, and scandium.

Analytical Chemistry.

Especial importance was attached at this time to a rational treatment of the chemical processes for the qualitative and quantitative determination of elements in their compounds. The beginnings of qualitative analysis, which we had occasion to describe in the former period, were continually more extended through the researches of Berzelius, Klaproth, and others, until they found a conclusion

in the present tables of chemical analysis, due to Pfaff, Rose, and especially to Remigius Fresenius. Analysis in the dry way also found no inconsiderable extension. As early as the phlogistic period the use of flame reactions was recommended by Marggraf. In 1820 the use of the blowpipe was introduced by Berzelius and Hausmann, while spectral analysis was discovered by Bunsen and Kirchhoff in 1859. Although Lavoisier, who introduced the use of the balance into chemistry, did not work out any practical method for the separation of inorganic compounds, yet useful methods of this description are due to Berzelius, Wöhler, Rose, and also especially to Fresenius. Volumetric analysis, introduced by Gay-Lussac in his introduction to chlorimetry (1824) and to alkalimetry (1828) was principally enriched in useful methods by Bunsen, Mohr, and Volhard. Some of these methods are still in general use. Gas analysis owes much to Bunsen, Winkler, and Hempel, as well as to the older chemists, such as Gay-Lussac, Dalton, Henry, etc.

The quantitative analysis of organic compounds worked out by Liebig was confined solely to those organic substances which contain carbon, hydrogen, and oxygen (*cf.* p. 135). Dumas in 1830 extended the scope of this kind of analysis by indicating a means for the accurate determination of nitrogen in organic compounds. The principle of this method was the measurement of the nitrogen as such. To Will and Varrentrapp* is due another method, in

* *Ann. der Chem.*, **39**, 257.

which the nitrogen is converted into ammonia, and in the form Kjeldahl* gave it this is still in general use. All these advances in the working out of useful analytical methods were also of great influence on the investigation of food and drugs, and on forensic chemistry. In this connexion may be especially mentioned Fresenius, Stas, Husemann, and König.

INORGANIC CHEMISTRY.

In considering the detailed advances in inorganic chemistry the increase in the number of elements is first to be mentioned. In the years 1860 and 1861 cæsium and rubidium were observed by Bunsen and Kirchhoff with the aid of spectrum analysis in lepidolite and in the mineral waters of Dürkheim, and were isolated therefrom. Gallium (1875) and indium (1863) were discovered in zinc ores, the former by Lecoq de Boisbaudran, the latter by Reich and Richter. Early in the forties Mosander discovered lanthanum, didymium, erbium, and thallium in the earth from Ytterby, and these were followed by the discovery of scandium by Nilson and of ytterbium by Marignac. Vanadium, known in combination from the beginning of the nineteenth century, was obtained in the free state, and recognized as an element by Roscoe in 1867. As was to be expected, the determination of the atomic weights of these new elements occupied the atten-

* *Zeitschrift für Analyt. Chemie*, **22**, 366; **24**, 455.

tion of various chemists, and the atomic weights of elements already known were also subjected to thorough examination. In this connexion these specially deserve mention: Bunsen, for indium, cæsium, and rubidium; Stas for sulphur, sodium, and potassium; Marignac for potassium, sodium, and metals of the alkaline earths; Crookes for thallium; and Winkler for aluminium, etc.

Careful attention was devoted to the occurrence of allotropy in the case of various elements, such as carbon, sulphur, and selenium. The transformation of ordinary phosphorus into the red modification, already observed by Berzelius, was fully studied in 1845 by Schrötter. The investigation of the crystalline forms of elements, like boron and silicon, hitherto known only in the amorphous condition, was carried out by Wöhler, and this was followed by the observation of amorphous and crystalline forms of chemical compounds, such as arsenious acid, mercuric iodide, and others. In 1842 ozone was discovered by Schönbein, and its composition and relation to oxygen were investigated by him, as well as by Marignac, De la Rive, Andrews, and Soret. Hand in hand with these researches went also the investigation of individual compounds of the different elements. On account of the narrow limits of this volume it is impossible even partially to catalogue the great number of newly prepared compounds in the province of inorganic chemistry. A short sketch of the most important will, therefore, only be given. Among the halogens, the exhaus-

tive researches of Gay-Lussac and others led in 1869 to the preparation of hydrofluoric acid in the pure state by Fremy and Gore, and in the same year Niklès fell a victim to the terrible effects of this compound. In addition to ozone as a strongly oxidizing agent, there was discovered hydrogen peroxide. The various stages of oxidation of the halogens, sulphur, nitrogen, phosphorus, and arsenic were subjected to closer study. Among the advances in the knowledge of metallic compounds the investigations on the action of light upon silver salts shall receive mention, as well as the application of this phenomenon for the fixation of light impressions. Boyle, Scheele, Ritter, and Davy (*cf.* p. 134) had already made observations in this connexion. To Daguerre and Talbot, however, is due the credit of having laid the foundations of photography, which has now reached so high a state of development. After Talbot had replaced the iodized silver plates by sensitive paper, Nièpce, Fry, and Archer in 1847 prepared negative pictures upon glass by the use of albumin or collodion.

Organic Chemistry.

An increase of the experimental material took place during this period still more among organic compounds than in the province of inorganic chemistry. This is not remarkable, for in the main all the theoretical developments, especially that of the doctrine of valency, were carried out upon

organic material. Here also, however, we must confine ourselves to a very cursory description of the progress in individual branches of the subject.

Among the hydrocarbons may be mentioned the syntheses by Wurtz,* the application of his reaction to aromatic compounds by Fittig, and the preparation of aromatic hydrocarbons by Friedel and Craft's method with the aid of aluminium chloride.† Exhaustive investigations by Baeyer on the constitution of benzene date from the years 1888 to 1890.‡ The carboxylic acids received exhaustive treatment: the saturated polybasic acids chiefly from Kolbe, and the unsaturated from Kekulé. The phthalic acids were closely studied in the course of Baeyer's work on benzene mentioned above. A general synthesis for the preparation of aromatic carboxylic acids with unsaturated side-chains was worked out by Perkin in the year 1877.§ Cahours indicated a general method for the preparation of acid chlorides by the action of phosphorus pentachloride on the acids,|| and the use of phosphorus trichloride instead of the pentachloride was recommended by Bécamp.¶ In continuation of this Gerhardt showed the way to the preparation of the anhydrides, while the formation of acid amides from the chlorides was already known to Liebig

* *Ann. Chim. Phys.*, [3], **44**, 273.
† *Ann. der Chem.*, **131**, 130.
‡ *Ibid.*, **245**, **251**, **256**, and **258**.
§ *Ibid.*, **147**, 230.
|| *Ann. Chim. Phys.*, [3], **37**, 285.
¶ *Comptes Rendus*, **40**, 944.

and Wöhler. The oxyacids were thoroughly investigated in the case of the lactic acids by J. Wislicenus, and they formed at the same time the subject of the manifold experiments of Pasteur which led to the establishment of Le Bel and van't Hoff's theory of optical isomerism (*cf.* p. 179). In the case of the oxyacids of benzene, the synthesis of salicylic acid discovered by Kolbe* in 1860 is of especial importance. Of the aldehydes and ketones, acetaldehyde and acetone were dealt with by Liebig. The constitution of the aldehydes was first proved by Kolbe, and as early as this time they were generally obtained by oxidation of the alcohols. Benzaldehyde was also (as has already been mentioned) investigated by Liebig in conjunction with Wöhler. Formaldehyde was, however, first obtained by A. W. Hofmann,† and the synthesis of ketones from acid chlorides and zinc alkyls is due to Williamson‡ (1852).

The action of chlorine upon acetic acid was studied by Dumas in connexion with his work on the phenomenon of substitution, and these researches gave occasion to numerous investigations on the action of chlorine and bromine upon hydrocarbons. In 1862 H. Müller observed the action of iodine as a chlorine carrier in the case of benzene and its homologues, and exhaustive investigations of this point were undertaken, especially by L. Meyer.

* *Ann. der Chem.*, **113** and **115**.
† *Proc. Royal Society*, **16**, 156.
‡ *Ann. der Chem.*, **81**, 86.

Among the aliphatic compounds, especially carboxylic acids, Hell and Volhard showed the application of amorphous phosphorus as a bromine carrier. The nitro-compounds were discovered in 1834 by Mitscherlich, who obtained nitrobenzene* by the action of nitric acid on benzene (*cf.* p. 138). By the action of sulphuric acid on benzene the same chemist in 1833 obtained benzene-sulphonic acid.†

Among organic nitrogen compounds we have seen that the amines (*cf.* p. 164) were for the first time closely investigated by A. W. Hofmann. In the aromatic series, azobenzene was first prepared by Mitscherlich‡ in 1853, azoxybenzene by Zinin,§ and hydrazobenzene in 1863 by A. W. Hofmann.|| In the year 1859 Peter Griess made the important discovery of the diazo - compounds, and in the theoretical consideration of these substances, in particular of the question of their constitution, Blomstrand and Kekulé took a share during this period. Among cyanogen compounds, hydrocyanic acid was investigated by Berthollet, the ferrocyanogen compounds and the sulphocyanogen compounds by Berzelius, and cyanic acid by Liebig. The alkylcyanides were first prepared by Dumas¶ in 1847 by treating the ammonium salts of the organic acids with phosphorus pentoxide, and their conversion into the corresponding carboxylic acids by means

* *Ann. der Chem.*, **12**, 305.

† *Pogg. Ann.*, **29**, 231; **31**, 628. ‡ *Ibid.*, **32**, 324.

§ *Ann. der Chem.*, **85**, 328.

|| *Jahresb. der Chemie*, 1863, 424.

¶ *Comptes Rend.*, **25**, 383, 442.

of potash was carried out by Kolbe and Frankland* in 1848. The isonitriles isomeric with them were predicted by Kolbe, and actually obtained in 1867 by A. W. Hofmann.† The latter also studied the alkyl compounds of the sulphocyanic acids, and in the light of this work he explained the constitution of the mustard oils.

Pyridine and quinoline, which were both known as early as the beginning of the last century, were soon recognized as constituents of various important vegetable alkaloids, and on this account they formed the object of numerous researches. The view which regards them as benzene and naphthalene respectively, in which one CH group is replaced by nitrogen, was first expressed by Körner, and in the experimental treatment of this subject it showed itself to be particularly fruitful.

The method of research due to Liebig and his contemporaries, which was experimental and yet also paid attention to theoretical considerations, undoubtedly has to record its greatest successes in the chemistry of the dyes. Here especially the success of an intimate combination of theory with practice has been shown. The dyeing industry, indeed, which at the middle of the last century did not exist, was by the year 1882 so highly developed that the total value of the dyes prepared in that year amounted to more than four millions sterling, of which about two-thirds falls to the German manufacturers, Germany being the country

* *Ann. der Chem.*, **65**, 269. † *Ibid.*, **144**, 144; **146**, 107.

in which the method of Liebig's school was chiefly practised. The first requisite for this successful development of the dyeing industry was the close study of the coal-tar produced in the manufacture of coal-gas as a by-product which at first was thought to be valueless. In 1834 Runge occupied himself with the examination of this substance, and later it was investigated in particular by A. W. Hofmann. Hofmann's researches on aniline in the years 1843 to 1845 especially may be termed the forerunners of the syntheses of the artificial dyes. The first chemical compound prepared in the laboratory which found employment as a dye was mauvein, obtained by Perkin in 1856. This was followed in 1858 by the synthesis of another, prepared by A. W. Hofmann by acting with tetrachloromethane on aniline, and in 1859 fuchsin was discovered by the French chemist Verguin at Lyons. Encouraged by these successes, chemists began to display feverish activity in the preparation of the most various dyes, and strove at the same time to exploit technically the new acquisitions to the fullest possible extent. In this way arose a great number of dye manufactories, of which there may be mentioned as the most important that at Höchst, that at Elberfeld, and the Badische Anilin- und Sodafabrik at Ludwigshafen.

The diazo-reaction of Griess rendered accessible the great class of the azo-dyes, the first representative being aniline yellow, discovered in 1863; and this was followed by Bismarck brown, discovered

in 1866 by Caro and Griess. Dimethyl aniline, first obtained by A. W. Hofmann, formed the starting-point for a series of dyes of the triphenylmethane group, such as malachite green, brilliant green, and others. The researches of Coupier and Rosenstiehl on the toluidines were quite indispensable for the preparation of dyes of the rosaniline group, and Baeyer's researches on benzene and the phthalic acids, which have already frequently been mentioned, led to fluorescein, eosin, phenolphthalein, etc.

In this way by degrees a great number of new dyestuffs were introduced into dyeing. On the other hand, chemists also strove to investigate the constitution of dyes already known, and for the most part of natural occurrence, in order to be able, by means of the knowledge so obtained, to synthesize them artificially from easily accessible compounds, and where possible to give such syntheses so cheap a form by the use of waste products from other branches of industry that the artificial dye might enter into successful competition with the natural product. We have a particularly prominent instance of this in the synthesis of indigo, known and prized as a dye even in antiquity. It may, therefore, be permissible to describe the growth of the indigo synthesis as an example, although a great deal of the work falls in point of time in the next chapter.

The investigation of the constitution of indigo is due to Baeyer, and the first synthesis of the dye was the result of his work. This was, however, no

immediate gain to its technical application, for anthranilic acid or *o*-nitrocinnamic acid, which were the starting-points in Baeyer's syntheses, and in the methods based on them which were worked out by Heumann and others, were so expensive that successful competition with the natural indigo was out of the question. It required an interval of nearly twenty years before the Badische Anilin- und Sodafabrik at Ludwigshafen succeeded in working out a promising method for the manufacture of anthranilic acid by the use of naphthalene, which was almost a waste product. This sealed the fate of natural indigo. In 1897 the production of artificial indigo was begun in Germany.*

The case has been similar with alizarin, the dye of madder, except that the working out of technically useful methods was accomplished much more easily than in the case of indigo. The first synthesis of alizarin is due to Graebe and Liebermann, and occurred in the year 1869.

Besides these researches, which have been of such great importance to technical chemistry, the chemistry of the dyes has also given occasion for a number of investigations, which at first possessed chiefly a theoretical interest, but by generalization soon became fundamental for all work in this subject. In the seventies E. Fischer began to occupy himself with the study of the relations of the rosaniline dyes, at that time still quite obscure,

* Recently other manufactories—*e.g.*, that of Höchst—have commenced the manufacture of indigo by their own processes.

and from his researches he was able to make clear, not only the progress of the reaction leading to the formation of these dyes, but also to explain satisfactorily their constitution. The determination with certainty of the constitution of different classes of dyes soon showed that an intimate relation must subsist between the chemical constitution of a compound and the nature of a dye. This raised the question as to what conditions the occurrence of colour in a chemical compound, and upon what rests its applicability as a dye. The study of the dyes from this point of view led to the establishment of a theory of dyes by O. N. Witt. This chemist supposed that the presence of certain atomic groups is the condition for the formation of a coloured compound, as well as for the power of such a substance to act as a dye.*

Chemical Manufacture.

From the description of the historical development of organic chemistry in general we have thus arrived at the description of the application of chemical reactions to chemical manufacture. It will be generally apparent that the rapid development of the dyestuff industry could not be without influence on the other branches of chemical manufacture. The enormous quantities of benzene, toluene, aniline, naphthalene, etc., which were needed for the preparation of the various dyes,

* O. N. Witt, *Ber. der Deutschen Chem. Ges.*, **9**, 522 (1875).

required the most careful working out of well-arranged apparatus for the distillation of coal-tar. Apart from the increased demand for hydrochloric acid, for nitric acid for nitrating, and for sulphuric acid for sulphonating, various other substances came from this cause for the first time into the list of products of chemical manufactories. To these belong especially sodium nitrite, which was required in large quantities for diazotizing the aromatic amines for the azo-dyes, and a great number of other substances, such as chromic acid or chromates, zinc chloride, sodium acetate, and many others. In the manufacture of coal-gas, the development of which was in general pretty well empirical—the first English works were erected in 1810—there is formed besides coal-tar another valuable waste product, the so-called 'gas liquor,' in which, as a result of the washing of the gas, the ammonia contained in it collects, and this liquid is worked up technically for ammonia and cyanogen compounds.

In the fermentation industry, the manufacture of spirit experienced great advances from the improvement of the apparatus for distillation. In the manufacture of vinegar the so-called 'quick vinegar process' rendered possible a rational mode of working. The process was first carried out by Schützenbach at Freiburg in 1823, and by Wagemann at Berlin in 1824. The manufacture of explosives, hitherto confined to the preparation of black gunpowder, was led into new paths by the discovery of gun-cotton in 1846 by Schönbein and Böttger.

The chemical nature and the extraordinary power of this explosive gave occasion for numerous investigations, in which Abel took the chief share. The process for utilizing nitroglycerine (which had long been known) in the form of dynamite was discovered by Nobel in 1862, and is of great importance. Matches tipped with a mixture of potassium chlorate and sulphur, and inflamed by being dipped into sulphuric acid, were introduced in 1807. They were replaced about the year 1833 by phosphorus matches inflamed by friction, and in 1848 a further improvement was effected by the use of non-poisonous red phosphorus instead of the poisonous yellow variety.

In the silicate industry the preparation of hydraulic mortar or cement may be specially mentioned. It received thorough investigation in respect of the hardening process at the hands of Winkler, Knapp, and others.

In the manufacture of paper the method for making paper from raw material of vegetable origin, such as wood and straw, was introduced successfully in 1846.

The researches of Liebig on the phosphates not only paved the way for the development of agricultural chemistry, but also founded the manufacture of artificial manures, and were at the same time not without influence on the beet-sugar industry.

The improvements in analytical methods rendered it possible to subject the impurities in iron to close examination, and this led to the working out of

practical methods for the production of the purest possible iron. The close investigation of the blast-furnace process by Rinmann and others, in conjunction with Bunsen's researches on the waste gases, rendered possible a clear perception of the relations between steel and iron. The introduction of the Bessemer process in 1856 was the first result of this work, and it was followed in 1879 by the Gilchrist and Thomas process for the removal of phosphorus. This process yielded also a waste product, the Thomas slag, which became, through the work of Wagner and others, a valuable manure in husbandry.

In the extraction of the other metals also various advances are to be recorded, especially in the case of nickel, when that metal came more and more into use as material for the manufacture of coins and utensils.

Chemical Instruction and Literature.

We have often had occasion in the course of this chapter to admire the success which followed the intimate co-operation of theory and practice. This success is not, perhaps, least to be ascribed to the care which during this period was devoted to the training of chemical students. At the beginning of the nineteenth century practically no laboratories for purposes of instruction were in existence, and the Chairs of Chemistry at the Universities were not independent, but were usually provided for as sub-

sidiary offices. Experimental lectures on chemistry were first delivered in France by Rouelle about the middle of the eighteenth century, and later they were introduced into England through the exertions of Davy. It was in England that Berzelius first heard them, and he was so convinced of their advantages that he himself employed them from the year 1812. In Germany their introduction did not take place so rapidly, on account of the dominating influence of natural philosophy at the time. They only became general towards the middle of the nineteenth century, thanks to the efforts of Liebig, Wöhler, Kolbe, Bunsen, and A. W. Hofmann.

To Liebig is undoubtedly due the credit of the development of practical instruction to the extent to which it is now carried out in all the places of higher education in Germany. It was he who emphasized the view that the centre of gravity of chemical study lies not in lectures, but in practical work. To him is due the systematic division of teaching into qualitative and quantitative analysis, the making of preparations, and the carrying out of independent investigations. Liebig's efforts in his teaching were chiefly directed to educating his pupils to make them capable of independent chemical thought. As time went on, all the places of higher education in Germany established laboratories in which the teaching of chemical students was arranged in this way, after the example of Giessen. This was accomplished at Göttingen by Wöhler in

the thirties, at Marburg by Bunsen in 1840, and at Leipzig by Erdmann in 1843.*

In other countries also we find similar institutions, though not at first to the same degree as in Germany, and this may furnish the reason why, as time went on, Germany took the first place in the treatment of chemical questions and in its influence on chemical manufacture.

Hand in hand with the development of practical instruction went also that of chemical literature. Large dictionaries, like those of Gmelin, Dammer, and Beilstein, appeared, in addition to text-books, such as those of Lavoisier, Thénard, Mitscherlich, Liebig, Wöhler, Regnault, Graham, and others. To supplement these there have arisen also dictionaries, such as those of Fehling or Ladenburg, or the *Dictionnaire de Chimie Pure et Appliqué* of Wurtz.

The continually increasing number of periodicals served to distribute as rapidly as possible the knowledge of new advances in chemical science. In France in 1878 the *Annales de Chimie* was founded by Berthollet, Lavoisier, and Fourcroy. From 1896 it has appeared under the name *Annales de Chimie*

* Although, as has been mentioned, the experimental lecture found a home in England before its introduction into Germany, yet rational chemical teaching was first properly provided in this country by the College of Chemistry, established in London in 1845. The German chemist A. W. Hofmann became its first professor (*cf.* p. 145), and the inspiration of his teaching there did much for chemical education in this country. The example set in this way has since been followed with more or less thoroughness by our other teaching institutions.—TRANSLATOR'S NOTE.

et de Physique. Since 1835 the *Comptes Rendus de l'Académie des Sciences* has been published in weekly parts by the French *Académie des Sciences.*

In England there existed at first the journals of the various learned societies, such as the *Philosophical Transactions* of the Royal Society. The chief organ at the present time is the *Journal of the Chemical Society,* which has appeared since 1848.

In Germany the first journal of this kind was the *Annalen der Physik und Chemie,* founded by Poggendorff in 1824; and this was followed by the *Annalen der Chemie und Pharmacie* of Liebig (1832), which since 1835 has borne the title of *Annalen der Chemie.* In 1828 the *Journal für Technische und Ökonomische Chemie* was founded by O. L. Erdmann, and this in 1834 appeared under the name *Journal für Praktische Chemie.* In 1868 the *Berichte der Deutschen Chemischen Gesellschaft* came into existence as the organ of the German Chemical Society. A *Zeitschrift für Chemie,* under the direction of Kekulé, Erlenmeyer, and Fittig, enjoyed a brief existence from 1857 to 1871. There were, besides, other journals more concerned with the publication of abstracts, such as the *Jahresberichte über die Fortschritte der Chemie,* the *Chemisches Zentralblatt,* and others.

Other countries also were not behindhand with publications of this kind. In most instances they are in connexion with academies or chemical societies—as, for instance, in Holland, Italy, Austria, Belgium, Russia, etc.

CHAPTER III

THE CHEMISTRY OF THE PRESENT DAY

In the preceding chapter we have been chiefly concerned with the historical development of organic chemistry, for during the period from 1830 to about the year 1885 that was the branch of chemical science which interested by far the greater number of chemists. The leading motive of their work was the endeavour to elucidate the constitution of organic compounds, and to obtain by systematic investigation a classification of them which should make it possible to comprehend the whole of this great, and at first sight difficult, subject.

The continually increasing number of cases of isomerism led to the development of structural chemistry, the most far-reaching conclusions of which are represented by the geometrical isomerism of J. Wislicenus and the optical isomerism of Le Bel and van't Hoff. The great stimulus which structural chemistry gave to chemical research is shown by the numerous successful syntheses of substances, the existence of which was to be predicted on structural chemical grounds. In the course of the last

fifty years the fruitfulness of synthetical chemistry on the basis of these ideas of structure has been shown in a very striking way. The syntheses of natural occurring products, which we have met with in the last chapter, continued to increase in number. Only a small part of them can be mentioned here—such as, for instance, the synthesis of alkaloids like coniine by Ladenburg in 1888, and the work on the alkaloids of opium carried out particularly in recent years by Freund, Pschorr, and Knorr. There may be mentioned further the researches of Emil Fischer on the sugars in the eighties and nineties, on uric acid in the nineties, and on the proteids at the present time. The successful treatment of the terpenes by Wallach and Baeyer may also be recalled, as well as the synthesis of various perfumes, such as vanillin, musk, and ionone. Various compounds have also been prepared which, by reason of their physiological effects, have entered into successful competition with drugs of natural occurrence. Instances are antipyrine (Knorr), phenacetin, pyramidon. The continually increasing number of artificial dyes, also, must not be forgotten. We have already in the preceding chapter become acquainted with indigo, the most important representative of this class.

The geometrical isomerism of J. Wislicenus, which has been mentioned above, sought to explain the different behaviour of substances like maleic and fumaric acids, or the two chlorpropylenes, as due to a different spacial arrangement of the atoms.

This assumption, first made only for carbon compounds, was applied by Hantzsch and Werner to nitrogen compounds in order to explain the occurrence of the phenomena of isomerism among the oximes and diazo-compounds.

The conception of optical isomerism became extended when not only optically active carbon compounds, but after the work of Le Bel (1889), Ladenburg (1892), and recently of Wedekind, optically active nitrogen compounds also became known. In 1900 the researches of Pope added to these optically active compounds of sulphur and of tin.

Especially important for the question of the constitution of organic compounds was the striking behaviour of some substances, which react in such a way that two different formulæ are required to explain fully their chemical properties, since they can react according to either of the two formulæ, although they actually exist only in one form. As a rule, these are compounds in which the atomic groups $-C(OH):C-$ or $-CO.CH_2-$ occur. Examples of this kind are the aceto-acetic esters, discovered by Geuther in 1863. Their reactions may be expressed by the two formulæ

$$CH_3.CO.CH_2.COOC_2H_5 \text{ and } CH_3.C(OH):CH.COOC_2H_5.$$

Other instances are isatin, carbostyril, cyanamide, etc. In the case of isatin, Baeyer terms the hydroxyl formula that of the stable modification, the keto-formula that of the labile form, which is not known in the free state, and only exists in the form of

derivatives. This is, according to him, the pseudo-form. C. Laar proposed for this phenomenon the term 'tautomerism,' and Victor Meyer the name 'desmotropy.' In time, however, the two tautomeric forms were actually isolated in several cases, and Dimroth has recently been able to prove conclusively that when tautomeric compounds are in the liquid condition or in solution both forms are present in equilibrium. The view expressed by W. Wislicenus that the phenomena of tautomerism are due to intramolecular reversible transformations has, therefore, proved to be correct, as also has the statement of J. Traube that tautomerism is a special kind of isomerism, in which we are dealing with two isomers which are easily transformed one into the other, and are in a state of equilibrium greatly influenced by external conditions. Elaborate investigations on tautomerism have been carried out in addition to the above-named chemists by Claisen, Hantzsch, Knorr, and Rabe. Of especial interest are the researches of Hantzsch on pseudo-acids and pseudo-bases, in which it has been shown that the salts have one and the free bases or acids the other of the two possible tautomeric forms (ionization-isomerism).

Organic Syntheses.

For the successful execution of all these important theoretical investigations the number of synthetical methods had necessarily to be increased. In this

connexion mention must first be made of a series of so-called condensations, which are carried out between aldehydes or ketones and certain reactive CH_2- or CH_3 groups under the influence of bases like caustic soda, sodium alcoholate, ammonia, piperidine, etc., or of acids such as hydrochloric acid or acetic acid. This work is due to Claisen, Knoevenagel, and others, with malonic ester and acetoacetic ester ; to Victor Meyer with benzyl cyanide ; and to various other chemists in the case of acetone, acetophenone, malonic nitrile, etc. The formation of hydrazones by the action of phenylhydrazine on aldehydes and ketones is also of importance. In the case of the oxyaldehydes and oxyketones this reaction leads to the production of osazones, as was discovered by Emil Fischer in 1884. The hydrazones, and especially their ortho-substitution products, were found to be distinguished by great reactivity, chiefly with formation of heterocyclic compounds, such as carbazol or triazin. The free hydrazine forms with acids hydrazides, from which Curtius in 1896 succeeded in preparing hydrazoic acid.

A similar reaction, generally characteristic of the aldehydes and ketones, is the action of hydroxylamine upon them, which was discovered by Victor Meyer in 1882 to 1883, and leads to the formation of oximes. These reactions also caused efforts to be made to render the aldehydes and ketones easily accessible by means of simple reactions. Although for the former, in spite of the aldehyde syntheses of Tiemann and Reimer, and in particular of Gatter-

mann, this problem has not yet been solved in a completely satisfactory manner, yet the aromatic ketones can be obtained comparatively easily in most cases, by Gattermann's method, from acid chlorides and benzene or its substitution products in the presence of aluminium chloride. The reactivity of aldehydes, ketones, and various derivatives of the acids, such as esters, chlorides, etc., with the organo-magnesium compounds has proved especially fruitful. The organo-magnesium compounds are easily prepared by the method discovered by Grignard in 1900. By this means it has been possible to obtain by a simple reaction secondary as well as tertiary alcohols, and from them ethene compounds by removal of water.

For the preparation of amino-acids the method of Gabriel has proved especially useful. It depends on the hydrolysis of the products arising from potassium phthalimide and the halogen fatty acids. The electrolytic reduction of aromatic nitro-compounds has been studied by various chemists—*e.g.*, Gattermann, Häussermann, Elbs, Tafel, etc. There may be obtained in this case, according to the experimental conditions, either azo-, azoxy-, and hydrazo-substances or amines and aminophenols. Other electrolytic work of a synthetic character, such as the synthesis of the higher dibasic acids, has been carried out by Miller, Brown, and Walker, and others. The general importance of the diazo-compounds discovered by Peter Griess in 1860 has been already mentioned in the preceding chapter.

Investigations of their constitution have been executed by Hantzsch and Bamberger in recent years. From the diazo-compounds phenyl haloids and phenyl nitriles can be easily obtained by the Sandmeyer reaction (1884 and following years), while by boiling with water phenols, or with alcohol hydrocarbons, can be prepared. Their reaction with primary or secondary amines leads to the formation of diazo-amino compounds and azo-dyes. The latter have already been mentioned on p. 196.

Physical Chemistry.

Taking into account isolated experiments of earlier date, the effort has made itself more and more felt during the last twenty-five years to study fully and accurately, in addition to synthetical organic problems, the reactions themselves in their individual stages—that is to say, to follow reactions as far as possible through their whole course. In many cases chemical operations no longer sufficed for this purpose, and it became necessary to seek more refined methods and more accurate apparatus, with the help of which to be in a position to follow the complete progress of a reaction. Assistance of this kind has been obtained from physics and physical measurements. At the same time, a general application of physical ideas to chemistry took place, and there followed accordingly a mutual fraternization, with the help of which many successful results were obtained. Mention need only be

made of thermo-dynamics and electro-chemistry. Owing to the good relations with physics, chemistry obtained in mathematics another associate. Efforts were made with the help of higher mathematics to express in formulæ the reaction itself, when its course has been elucidated, and in this way it was defined in the most precise manner possible. With such endeavours that branch of chemical science is occupied which we now term 'physical' or 'general chemistry.' Through the efforts of men like Gibbs, van der Waals, van't Hoff, Ostwald, and others, it has worked its way from small beginnings to a science of the first importance.

The beginning of the chemistry of the present day is placed in the year 1886, and so in that year in which Svante Arrhenius published his theory of electrolytic dissociation. For the purpose of describing this very fruitful theory we must go back a little in point of time. In the year 1877 the botanist Pfeffer carried out a series of investigations on the osmotic pressure of sugar solutions with the aid of the semipermeable membranes discovered in 1867 by Traube. Reasoning from this work, van't Hoff developed the idea that the osmotic pressure is generated by the impact of the dissolved molecules on the walls, and so came to the conclusion that the state of a dissolved substance bears a great similarity to that of a gas, and that consequently the gas laws, including Boyle's law, Gay-Lussac's law, and Avogadro's hypothesis, could be applied directly to solutions. The extension of these

researches of van't Hoff yielded us the methods for determining molecular weights with the aid of the lowering of vapour pressure, depression of freezing-point, and elevation of boiling-point, which are rendered practicable in the forms worked out by Raoult and Beckmann. In employing these methods, Raoult, and after him several other chemists, found that solutions of salts, acids, and bases do not obey this law of van't Hoff, but that, on the contrary, their molecular weights are always found too small —generally only a half or a third of the expected value. As a result of this, the validity of van't Hoff's theory was naturally placed very much in question, and he was compelled to support it by additional hypotheses. Then Arrhenius showed that only those solutions which are electrolytes fail to agree with van't Hoff's theory. These are the solutions which conduct the electric current, and are, according to Faraday, split up by it into their ions. This fact led Arrhenius to the supposition that this separation into ions is not first produced by the electric current, but that, on the contrary, the ions are already present in the aqueous solution. The splitting of electrolytes into their ions under the influence of water as a solvent was termed 'dissociation.' The extent of the dissociation varies, and depends essentially upon the degree of dilution. For its determination a simple means was offered by the measurement of the electrical conductivity, which is relatively easily carried out. The example in this direction was set by Arrhenius himself, and

then received considerable improvements at the hands of Planck, Ostwald, Kohlrausch, and others.

A whole series of phenomena which had previously been obscure found a simple explanation on this theory—as, for instance, the identity of the heat of neutralization of one and the same acid with different bases, and *vice versa*, and consequently many new and fruitful ideas developed out of it. Electro-chemistry itself experienced as a result of this many changes and extensions. W. Nernst, for instance, succeeded by means of it, in conjunction with van't Hoff's theory of solution and his own theory of diffusion, in giving a satisfactory theory of the voltaic cell, and so solving a problem a hundred years old. The researches on concentration cells, oxidation and reduction cells, the determination of the electro-motive behaviour in general of the most various substances, the determination of the conductivity of a great number of acids and bases, and the so-called affinity constants derived from this—all these stand on the basis of the theory of ions in aqueous solution. Electro-chemistry, which had been hitherto a more or less unknown subject, obtained pith and value in this way, and its practical development also was greatly assisted. Electro-chemical reactions were brought into use in analytical chemical practice, both for qualitative and for quantitative analysis. In this connexion may be mentioned the names of Classen, Miller, and Kiliani. In chemical manufacture electricity is now applied in chemical reactions in numerous instances.

The electrolysis of the alkaline chlorides, which leads to the preparation of the caustic alkalis and to the isolation of chlorine ; the electrolytic preparation of hypochlorites ; the electro-chemical processes of extraction for the metals—*e.g.*, copper, zinc, magnesium, aluminium, etc.—and the extensive electro-syntheses of organic compounds, particularly the reduction of the nitro-compounds, etc., are eloquent examples of the extensive use of electrical energy in chemical manufacturing. Finally, various experiments have been carried out by Moissan at very high temperatures (2,000° to 3,000°), the temperatures being conveniently attained by the use of the electric furnace. The results of this work have been the preparation of artificial diamonds, the isolation of fluorine, and especially the practically valuable formation of calcium carbide, the starting-point for the preparation of acetylene.

Inorganic Chemistry.

If we now leave electro-chemistry and turn again to purely chemical questions which have been dealt with in recent years, there may be mentioned in connexion with Moissan's thermo-electric researches the Goldschmidt process for the production of high temperatures by means of aluminium powder. By this means it is possible to obtain metals like iron, chromium, manganese, etc., free from carbon. In contrast with this work may be mentioned the method discovered by Linde in 1895 for the pro-

duction of low temperatures, especially for the liquefaction of atmospheric air. In this way temperatures in the neighbourhood of $-190°$ can be easily obtained. Besides Linde, the compression of gases has engaged the attention especially of Pictet, Cailletet, Wroblesky, and Dewar.

The number of known elements was increased in 1894 and the following years by the inert gases argon, helium, xenon, krypton, and neon, discovered by W. Ramsay and Lord Rayleigh. The discovery of argon was due to the different specific gravity of the nitrogen obtained from air and that prepared by oxidation from ammonia. Helium was discovered by Ramsay as a gas evolved when the mineral cleveite is treated with sulphuric acid.

In 1869 Hittorf made the discovery that peculiar rays proceed from the cathode of a highly evacuated discharge tube, and he termed them 'cathode rays.' These rays aroused general attention when their remarkable effects became known through the work of Röntgen in 1895. The further investigations of numerous physicists led to the rays being ascribed to the movement of negatively charged material particles, the electrons. This is only mentioned here because recently the conception of electrons has also found entry into chemistry, so that it is attempted to regard the ions as compounds of the atoms or atomic complexes concerned with the electron. In 1896 Becquerel observed that the power of the cathode rays of causing barium platinocyanide to fluoresce, or of making air con-

duct, was also possessed by certain minerals, in particular by natural pitchblende. M. and Mme. Curie succeeded with great labour in isolating from this pitchblende the bromide of a new element, which they termed 'radium.' Various other elements were found besides radium which were carriers of this particular radiant energy—*e.g.*, radio-tellurium, radio-lead, and radio-bismuth. It is especially interesting that in the case of these substances, owing to the emission of the so-called emanation, a continual loss of energy occurs, and, most remarkable of all, Ramsay has observed that the emanation becomes transformed into helium.

Among the other elements and their compounds extensive improvements in modes of preparation are to be noted. The contact process for the preparation of sulphuric acid, discovered by Peragrine Phillips in 1831, was introduced into manufacture by Winkler in 1875, and was developed by Knietsch to such an extent that it is possible to prepare it directly from the gases from the roasting kilns. As calculation shows that the saltpetre deposits in Chile will be exhausted at a time now within sight, attention has recently been paid to the old idea of preparing nitric acid from the nitrogen of the air. There is every appearance that a successful form of this process is about to be perfected. There are, at any rate, now two factories in Norway, where the preparation of nitric acid from the air with the help of the electric current is being carried on. The lighting industry has experienced considerable

development through the discovery of Auer von Welsbach of the use of the oxides of thorium and cerium for the purpose of making luminous the non-luminous flame of the Bunsen burner. In this way a light has been obtained which, on account of its intensity and cheapness, successfully competes with the electric light.

The manifold applications of electrical energy to chemical operations have already been mentioned. It has proved especially valuable for the purpose of covering certain base metals, or plaster casts, with a thin and regular layer of a noble metal, such as gold or silver, or of any other metal—*e.g.*, nickel, copper, etc. This kind of gilding or silvering is termed 'galvano-plastic.'

VALENCY.

In the last chapter we have seen that chemists were not able to agree upon the question of the constant or changing valency of the elements. The supporters of the former view, in logically carrying out their theory, had to take refuge in a doubling of certain formulæ. Thus, they wrote ferrous chloride Fe_2Cl_4, cuprous chloride Cu_2Cl_2, and mercurous chloride Hg_2Cl_2. By means of Victor Meyer's method of vapour density determination (*cf.* p. 184) it was proved, however, that these compounds do exist (although only in the form of vapour) as $FeCl_2$ and HgCl, so that a change of valency must be unconditionally admitted. Another fact also speaks

in favour of this view—namely, that oxygen, which is otherwise always divalent, can, under some circumstances, be tetravalent. This follows from the observations of Baeyer on the addition of acids to certain compounds containing oxygen, such as pyrone, xanthone, etc. On the ground of extensive researches on the so-called carbon double linkage, with special reference to benzene derivatives, J. Thiele maintains the divisibility of valency, assuming the possibility of so-called partial valencies.* In the closing years of the past century A. Werner, as a result of researches on the cobaltiac compounds, extended the conception of valency by assuming a limiting number (obtained by introduction of the so-called co-ordination number) which expresses the number of atoms that can be in direct union with a given other elementary atom independently of the valency number. The work of Abegg and Bodländer† may also be mentioned. On the ground of the supposition referred to on p. 217, that the ions are saturated compounds of the elementary atoms with the electron, they sought to apply the so-called electric affinity of the individual elements to the conception of valency.‡ Here also we are at present faced with a field of work which cannot in any way be regarded as even approximately worked out.

* *Ann. der Chem.*, **306** *et seq.*

† *Zeitschrift für Anorg. Chem.*, **20**, **453**.

‡ Abegg, *ibid.*, **36**, 330 *et seq.*

Chemical Instruction and Literature.

The method of chemical instruction which proved so successful in the middle of the nineteenth century brought with it a steady increase in the chemical laboratories at the Universities and other places of higher education. There may here find mention in this connexion the chemical department of the University of Berlin, opened in 1898, and the department for physical chemistry of the University of Leipzig, opened in 1896.

The enormous growth of every individual part of chemical science was naturally accompanied by an ever greater specialization. This may, perhaps, be most plainly seen in the literature. Apart from the great number of text-books and handbooks on the different branches of chemistry, a very great increase is also found in the periodicals devoted to special subjects. So arose the *Zeitschrift für Anorganische Chemie* (1892); the *Zeitschrift für Physikalische Chemie*, edited by van't Hoff and Ostwald (1887); the *Zeitschrift für Physiologische Chemie*, edited by Hoppe-Seyler (1877); the *Zeitschrift für Analytische Chemie*, founded by R. Fresenius (1862); the *Zeitschrift für Angewandte Chemie*, published by the *Verein Deutscher Chemiker;* and the *Zeitschrift für Electrochemie*, the organ of the *Deutsche Bunsengesellschaft für Angewandte Physikalische Chemie*. The possibility of extensive exchange of opinions on scientific questions is provided for by the establishment of a number of congresses. Recently the

effort has also made itself felt to give life to the study of the history of chemistry by the publication of collections of important original researches or of the correspondence of the earlier chemists. In this connexion the chief credit is due to W. Ostwald and J. Kahlbaum. In the same way these pages, which can only present a short and incomplete course through the history of chemistry, may furnish an incitement to young chemists and students of chemistry to penetrate further into the origins and growth of chemical science.

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BILLING AND SONS, LTD., PRINTERS, GUILDFORD.